

03-0210



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:  
C. DANIEL MCCLAIN

Serial No.: 09/578,001

Group Art Unit: 1714

Filed: May 24, 2000

Examiner: Antionette Sanders-Kriellion

For: Method and Apparatus for  
Producing and Aqueous  
Paint Composition from a  
Plurality of Premixed  
Composition

Commissioner for Patents  
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OK to Enter  
Mr. GREGORY MILLS  
4/7/05  
QUALITY ASSURANCE SPECIALIST

**PROTEST UNDER 37 C.F.R. § 1.291**

**I. Summary**

Rohm and Haas Company (“Rohm and Haas”) of Philadelphia, Pennsylvania submits this protest against this application pursuant to 37 C.F.R. § 1.291. We have been informed by MicroBlend Technologies, Inc. (“MicroBlend”), the owner of this application, that in October, 2003 it copied claims from a Rohm and Haas patent (U.S. Patent No. 6,531,537 (“the ‘537 patent”)) into this application and that MicroBlend has requested an interference between this application and the ‘537 patent based on the copied claims. In order for the USPTO to declare an interference, there must be subject matter claimed in the above-identified application that is patentable to MicroBlend.

On December 27, 2004, MicroBlend filed a request for *inter partes* re-examination of the ‘537 patent, stating that the allegedly interfering subject matter is unpatentable over art (e.g., U.S. Patent No. 5,672,649 and Canadian Patent No. 2,166,290) that is prior art to both the ‘537 patent and this application. MicroBlend’s unpatentability statements in that re-examination

request – summarized below – are admissions of unpatentability by MicroBlend that the Examiner should use under 37 C.F.R. §1.104(c)(3) and M.P.E.P. 706 to reject the copied subject matter in this case (“[i]n rejecting claims the examiner may rely upon admissions by the applicant . . . in a reexamination proceeding, as to any matter affecting patentability”). Because MicroBlend now states that the allegedly interfering subject matter is unpatentable, no interference can be declared. 37 C.F.R. §§ 41.102(a) and 41.102(b)(1); *see also*, 37 C.F.R. §§ 41.202(c)(1) and (c)(2). Rohm and Haas requests that notice be sent to it and to MicroBlend that no interference will be declared.

## **II. Procedural Background**

MicroBlend is the owner or real party-in-interest of this application.<sup>1</sup> Rohm and Haas and MicroBlend are presently in litigation in the United States District Court for the Central District of California. Rohm and Haas sued MicroBlend for infringing claim 6 of the ‘537 patent.

MicroBlend informed the Court and Rohm and Haas that it copied numerous claims including claim 6 of the ‘537 patent into this application in an attempt to provoke an interference with the ‘537 patent. MicroBlend moved to stay the litigation pending USPTO determination of its request for an interference between the ‘537 patent and this application. The Court granted MicroBlend’s request for a stay on July 23, 2004.

On December 27, 2004, MicroBlend filed a request for *inter partes* re-examination of the ‘537 patent. That re-examination request (Control Number 95/000,068) is assigned to Examiner Tae Yoon. In that request, MicroBlend states that the claims of the ‘537 patent are unpatentable. These are the same claims that MicroBlend has copied into this application.

## **III. Rohm and Haas’ Compliance with The Procedural Aspects of Rule 1.291**

This protest identifies the patent application to which it pertains. Rule 1.291(a). This protest is being submitted prior to the date the application was published or allowed,<sup>2</sup> and a copy

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<sup>1</sup> See assignment records of U.S. Patent 6,221,145 recorded at Reel/Frame 009683/0567 on 12/23/1998 and recorded at Reel/Frame 014373/0547 recorded 8/13/2003. The above-identified application is a continuation-in-part of the application that issued as U.S. Patent 6,221,145.

<sup>2</sup> Upon information and belief, a notice of allowance was mailed on or about July 28, 2003 for subject matter that is different than the allegedly interfering subject matter. On or about October 9, 2003, MicroBlend filed a Request for

of this protest is being served upon the applicant in accordance with § 1.248. Rule 1.291(b). This is the first protest submitted in this application by Rohm and Haas, the real party in interest who is submitting it. Rule 1.291(b)(2). The patents cited by MicroBlend in its re-examination request and a copy of the re-examination request itself are enclosed. Rule 1.291(c)(3). The materials submitted with this protest are in English. Thus, no English language translations are necessary Rule 1.291(c)(4).

**IV. Rohm and Haas' Compliance with The Substantive Aspects of Rule 1.291 – Listing of Patents, Publications, and Other Information Relied Upon (i.e., the Admissions By MicroBlend in its Re-examination Request)**

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Rohm and Haas submits the following substantive information in connection with this protest:

- a. MicroBlend's Request for *inter partes* Re-examination of U.S. Patent No. 6,531,537 containing MicroBlend's admissions. (Exhibit A)
- b. The Art Cited By MicroBlend in the re-examination Request:
  - Brock U.S. Patent No. 5,672,649 ("Brock") (Exhibit B)
  - Heuwinkel CA 2,166,290 ("Heuwinkel") with cover page of corresponding publication WO 95/029960 (Exhibit C)
  - Falcoff U.S. 4,403,866 ("Falcoff") (Exhibit D)
  - Brown U.S. 5,521,234 ("Brown") (Exhibit E)
  - Kitano U.S. 4,436,845 ("Kitano") (Exhibit F)
  - Sperry U.S. 4,243,430 ("Sperry") (Exhibit G)
  - Kowalski U.S. 4,880,842 ("Kowalski") (Exhibit H)
  - Bauer U.S. 5,989,331 ("Bauer") (Exhibit I)
  - Pyves CA 935,255 ("Pyves") (Exhibit J)
  - Landy U.S. 5,527,853 ("Landy") (Exhibit K)
  - Tsuei U.S. 5,643,669 ("Tsuei") (Exhibit L)

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Continuation Examination wherein MicroBlend copied claims from the '537 patent into this application. No notice of allowance of that copied subject matter has been mailed.

**Rohm and Haas' Compliance with Rule 1.291 – Concise Statement of the Relevance of MicroBlend's Admissions**

In its *inter partes* re-examination request (Control No. 95/000,068; EXHIBIT A), MicroBlend states that all 50 claims of the '537 patent are unpatentable, relying on art that is prior art to this patent application. MicroBlend's statements in its re-examination request are admissions by MicroBlend that can be used against MicroBlend to reject its claims in this application. 37 CFR § 1.104(c)(3).<sup>3</sup>

MicroBlend's admissions<sup>4</sup> regarding the unpatentability of each copied claim of the '537 patent include the following:

<b>Copied Claim of the '537 Patent</b>	<b>MicroBlend Admissions</b>	<b>Where Admitted</b>
1	Anticipated by Brock & Heuwinkel (Exhibits B and C).	Reexamination Request (“Request”) at pages 21–22.
2	Anticipated by Brock & Heuwinkel (Exhibits B and C).	Request at page 23.
3	Anticipated by Brock & Heuwinkel (Exhibits B and C).	Request at page 23.
4	Anticipated by Brock & Heuwinkel (Exhibits B and C).	Request at page 24.

<sup>3</sup> MicroBlend's statements are not an admission by Rohm & Haas. Rohm & Haas reserves the right to dispute any statement by MicroBlend, the USPTO, or any third party that the claims of the '537 patent are unpatentable to Rohm & Haas.

<sup>4</sup> MicroBlend also relies on its own patent, U.S. 6,221,145 (“the '145 patent”). Rohm & Haas has not included MicroBlend's statements regarding the '145 patent in this table. The above-identified application claims priority to the application from which this patent issued. Rohm & Haas does not concede that the above-identified application is entitled to the filing date of the application that issued as the '145 patent.

Copied Claim of the '537 Patent	MicroBlend Admissions	Where Admitted
5	Anticipated by Brock & Heuwinkel (Exhibits B and C). Alternatively, obvious over Brock or Heuwinkel in view of Falcoff (Exhibit D).	Request at page 24.
6	Anticipated by Brock & Heuwinkel (Exhibits B and C). Alternatively, obvious over Brock or Heuwinkel in view of Falcoff (Exhibit D).	Request at pages 25–27.
7	Anticipated by Brock & Heuwinkel (Exhibits B and C). Alternatively, obvious over Brock or Heuwinkel in view of Falcoff (Exhibit D).	Request at page 27.
8	See claim 7.	Request at page 27.
9	Unpatentable over Brock, Heuwinkel and Brown. (Exhibits B, C and E).	Request at page 27.
10	See claims 7, 8 and 9.	Request at page 28.
11	Unpatentable over Heuwinkel, Brock, and Falcoff (Exhibits B-D).	Request at page 28.
12	Obvious over Brock or Heuwinkel in view of Kitano (Exhibits B, C and F).	Request at page 28.

<b>Copied Claim of the '537 Patent</b>	<b>MicroBlend Admissions</b>	<b>Where Admitted</b>
13	Unpatentable over Brock or Heuwinkel (Exhibits B and C).	Request at page 28.
14	Unpatentable over Brock, Heuwinkel or Falcoff (Exhibits B-D).	Request at page 28.
15	See claim 3.	Request at page 29.
16	See claim 4.	Request at page 29.
17	Unpatentable over Brock, Heuwinkel, or Falcoff. (Exhibits B-D).	Request at page 29.
18	See claim 2.	Request at page 29.
19	Unpatentable over Brock, Heuwinkel, or Tsuei. (Exhibits B, C and L).	Request at pages 29–30.
20	See claim 19.	Request at page 31.
21	Unpatentable over Brock, Heuwinkel, and Tsuei (Exhibits B, C and L).	Request at page 31.
22	See claim 21	Request at page 23.
23	See claim 3.	Request at page 32.
24	See claim 1. MicroBlend also relies on Brown, Kitano, Sperry, and Kowalski (Exhibits E–H).	Request at page 32.
25	See claim 24.	Request at page 32.

<b>Copied Claim of the '537 Patent</b>	<b>MicroBlend Admissions</b>	<b>Where Admitted</b>
26	See claim 24. MicroBlend also relies on Kowalski and Brock (Exhibits B and H).	Request at page 33.
27	Unpatentable over Bauer, Brock & Heuwinkel (Exhibits I, B and C).	Request at page 33.
28	MicroBlend admits unpatentability over a number of references including Pyves, Brock and Heuwinkel (Exhibits J, B and C).	Request at page 33.
29	See claim 1.	Request at page 34.
30	Unpatentable over Brock, Heuwinkel, Falcoff, Pyves, and Bauer (Exhibits B, C, D, J and I).	Request at page 34.
31	Anticipated by Brock and Heuwinkel. (Exhibits B and C).	Request at pages 34–36.
32	Anticipated or obvious over Brock and Heuwinkel (Exhibits B and C).	Request at pages 36–37.
33	Anticipated or obvious over Brock and Heuwinkel. (Exhibits B and C).	Request at page 37.
34	Unpatentable over Brock or Heuwinkel. (Exhibits B and C).	Request at page 38.

Copied Claim of the '537 Patent	MicroBlend Admissions	Where Admitted
35	See claims 1, 32, and 31.	Request at page 38.
36	See claim 31.	Request at page 39.
37	Anticipated by Brock or Heuwinkel or obvious over Brock or Heuwinkel (Exhibits B and C).	Request at page 39.
38	See claim 5.	Request at pages 39–40.
39	See claim 1.	Request at page 40.
40	See claims 1, 5, and 39.	Request at pages 40–41.
41	See claims 1, 6 and 39.	Request at pages 41–42.
42	Obvious over Brock or Heuwinkel in light of Kitano (Exhibits B, C, and F). See also Tsuei (Exhibit L).	Request at page 42.
43	See claims 1, 5, and 42.	Request at page 43.
44	See claims 1, 6, and 42.	Request at pages 43–44.
45	See claim 1.	Request at pages 44–45.
46	See claims 1 and 39.	Request at pages 45–46.
47	See claim 6. Obvious over Brock or Heuwinkel. (Exhibits B and C).	Request at page 47.
48	See claim 5, 45, 46 and 47.	Request at page 47.
49	See claim 31.	Request at page 47.
50	See claim 31.	Request at page 47.

MicroBlend also made the following admissions:

... ‘537 patent claims 1 – 50 are invalid under either 35 U.S.C. § 102 or § 103 because they are anticipated or made obvious . . . by U.S. Patent No. 5,672,649 to Brock et al. (hereinafter “Brock”), issued September 30, 1997 . . . by Canadian Patent No. 2,166,290 to Heuwinkel et al. (hereinafter “Heuwinkel”), published November 9, 1995 as International Publication No. WO 95/29960 . . . , and by other prior art references (Request at page 4).

The Friel ‘537 patent claims are invalid because each element of every claim is anticipated by or made obvious by the disclosure of . . . Brock, Heuwinkel, and other various prior art references taken alone or in combination (Request at page 8.).

MicroBlend makes an extensive statement about unpatentability over Brock. See Request at pages 13–16. MicroBlend specifically stated that copied claims 1, 5 and 6 are anticipated by Brock. See Request at page 15.

MicroBlend makes an extensive statement about unpatentability over Heuwinkel. See Request at pages 17–19. MicroBlend specifically stated that copied claims 1, 5 and 6 are anticipated by Heuwinkel. See Request at page 19.

Because MicroBlend has admitted that the copied claims are unpatentable to MicroBlend, no interference should be declared. 37 C.F.R. §§ 41.102(a) and 41.102(b)(1).

#### V. Conclusion

MicroBlend’s statements in its *inter partes* reexamination request are admissions by MicroBlend that the claims it copied from the ‘537 patent are unpatentable to MicroBlend. 37 C.F.R. 1.104(c)(3), M.P.E.P. 706. Because MicroBlend admits that the subject matter of the copied claims is unpatentable, no interference can be declared. 37 C.F.R. §§ 41.102(a) and

41.102(b)(1) *see also*, 37 C.F.R. §§ 41.202(c)(1) and (c)(2).

Respectfully submitted,

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February 25, 2005

382028\_2.DOC

**CERTIFICATE OF SERVICE**

I, Gerard M. O'Rourke, do hereby certify that on March 1, 2005, I caused copies of the  
**PROTEST UNDER 37 C.F.R. § 1.291** to be delivered via Federal Express to the following  
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EXHIBIT

A

**IN THE UNITED STATES PATENT  
AND TRADEMARK OFFICE**

**REQUEST FOR REEXAMINATION OF  
UNITED STATES PATENT NO. 6,531,537**

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## I. BACKGROUND

This is a request for reexamination of U.S. Patent No. 6,531,537 to Friel et al. (the “537 patent”, Exhibit A). The ‘537 patent is currently being considered by the Office for interference with U.S. Patent Application Serial No. 09/578,001 to McClain et al. The most recent Office Action rejected the claims corresponding to copied claims 19, 20 and 22 from the ‘537 patent based upon U.S. Patent Number 5,643,669 to Tsuei (hereinafter “Tsuei”). Tsuei was not cited during the prosecution of the ‘537 patent.

The present request for reexamination is compelled by a detailed review of the claims of the ‘537 patent in relation to prior art references in light of a patent infringement suit filed by Rohm & Haas Company (“Rohm & Haas”), the owner of the ‘537 patent, in the United States District Court for the Central District of California Western Division, against the Requestor, MicroBlend Technologies, Inc. (“MicroBlend”).

During prosecution of the ‘537 patent, no less than seven information disclosure statements were filed with the Office, and no rejections based upon prior art were made against the very broad claims that issued. When faced with a patent infringement suit, MicroBlend was surprised to find that Rohm & Haas was suing MicroBlend for infringement of the ‘537 patent by a product similar to that described in a MicroBlend patent filed approximately 14 months prior to Rohm & Haas’ earliest priority date and referenced on the face of the ‘537 patent. Though no “publication” with full disclosure has been found, products like those described in MicroBlend’s patent were on sale more than one year prior to the earliest priority date for the ‘537 patent. Further review of

relevant prior art, including references cited in the '537 patent, revealed that many other patents clearly render the issued claims invalid but were not applied to the '537 patent claims by the Patent Office. Despite the earlier priority dates and the materiality of the disclosures to the pending claims, no rejection of the '537 patent claims was made by the Office relying upon any cited prior art.

Reexamination is requested because '537 patent claims 1-50 are invalid under either 35 U.S.C. § 102 or § 103 because they are anticipated or made obvious by U.S. Patent No. 6,221,145 to McClain (hereinafter "McClain") filed December 23, 1998 and issued April 24, 2001 (Exhibit C), by U.S. Patent No. 5,672,649 to Brock et al. (hereinafter "Brock"), issued September 30, 1997 (Exhibit D), by Canadian Patent No. 2,166,290 to Heuwinkel et al. (hereinafter "Heuwinkel"), published on November 9, 1995 as International Publication No. WO 95/29960 (Exhibit E), and by other prior art references. Therefore, reexamination under 35 U.S.C. §§ 302-307 and 37 C.F.R. § 1.510 et seq. is requested of all claims of the '537 patent.

A detailed explanation of the '537 patent scope, the prior art and the claim charts that show how the prior art applies to each claim of the '537 patent is set forth below.

## II. THE FRIEL '537 PATENT

### A. The Friel '537 Patent Requires a Set of Different Fluid Prepaints Which Form Paint When Mixed Together

The '537 patent is directed to a plurality of mutually compatible fluid compositions that are not paint prior to mixing, but which form paint when mixed together. By mixing these "prepaints" together in varying ratios, a variety of paints may be formed with differing characteristics and qualities. '537 patent, col. 3, lines 16-49 and col. 4, lines 35-41, Exhibit A.

The three main prepaint components of the '537 patent are: 1) an opacifying prepaint comprising an opacifying pigment; 2) an extender prepaint comprising an extender pigment; and 3) a binder prepaint comprising a latex polymeric binder. The '537 patent broadly describes each of its components and claim terms, and includes long lists of alternative chemicals to be used in each of the prepaint components. To better understand the intended scope of the '537 patent claims, each of the prepaints are explained below with definitions from the '537 patent and from the common knowledge available within the relevant art.

### B. An Opacifying Prepaint Comprises an Opacifying Pigment

Although the term "opacifying prepaint" itself is not specifically defined in the '537 patent, extensive examples and descriptions of opacifying pigments which make the prepaint an opacifying prepaint are included. The '537 patent states at col. 10, lines 8-25, Exhibit A:

**Suitable opacifying pigments include white pigments which impart white scattering power to the paint across all visible wavelengths without a high degree of absorption. . . . Suitable opacifying pigments include titanium dioxide (TiO<sub>2</sub>) or a combination of titanium dioxide and auxiliary hiding pigments such as voided latex polymer particles, zinc oxide, lead oxide, a synthetic polymer pigment and mixtures thereof. Rutile and anatase grades of titanium dioxide are suitable for use herein. Rutile titanium dioxide is preferred. The surface of these titanium dioxides may be treated with various organic surface treatments and/or inorganic surface treatments, e.g., treatment with the oxides of silica, alumina and zirconia. Fumed titanium oxide is also useful herein.**

Emphasis was added to identify particularly important terms for use in later discussion.

### **C. An Extender Prepaint Comprises an Extender Pigment**

Although the term "extender prepaint" itself is not specifically defined in the '537 patent, extensive examples and descriptions of extender pigments which make the prepaint an extender prepaint are included. The '537 patent states at col. 10, line 53 to col. 11, line 2, Exhibit A:

Extender pigments useful herein include exterior and interior extender pigments optimized for the intended end use. Exterior extender pigments are not soluble in water and have a low absorption number. They are optimized for exterior durability in the particular market where the paint will be sold, and they do not detract from the desired non-cracking, non-chalking, and non-dirt-retaining properties of the dried paint. They also provide volume at a low cost. Interior extender pigments are optimized for hiding, gloss, and low cost. **Suitable extender pigments include barium sulfate (1-15 microns), Blanc Fixe (0.5-5 microns), calcium carbonate (0.05-35 microns), silica (0.001-14 microns), magnesium silicate (0.5-15 microns), aluminum silicate (0.2-5 microns), nepheline syenite, mica, bentonite, magnesium alumino-silicate, fumed butylen, colloidal attapulgite, synthetic amorphous sodium alumino-silicate, sodium potassium alumino-silicate, and the like.**

Emphasis was added to identify particularly important terms for use in later discussion.

#### **D. A Binder Prepaint Comprises a Latex Polymeric Binder**

Although the term "binder prepaint" itself is not specifically defined in the '537 patent, extensive examples and descriptions of latex polymeric binders which make the prepaint a binder prepaint are included. The '537 patent states at col. 11, lines 3-59,

Exhibit A:

**Latex polymeric binders are polymers or prepolymers which form the primary paint film.** They bind the pigment and/or extenders, provide the required paint flow, and determine the gloss and hardness of the final paint film. The binders selected for the prepaints will depend upon the final use of the formulated paints. Binders suitable for exterior paints are generally suitable for interior paints, but binders suitable for interior paints may not be suitable for exterior paints.

Suitable latex polymeric binders include, but are not limited to, homopolymers, copolymers or terpolymers such as, for example, **acrylic and/or methacrylic polymers** or copolymers, polyvinyl acetate, styrene-acrylic copolymers, styrene-butadiene, vinyl acetate-acrylic copolymers, ethylene-vinyl acetate copolymers, vinyl acetate-vinyl versatate copolymers, vinyl acetate-vinyl maleate copolymers, vinyl acetate-vinyl chloride-acrylic terpolymers, ethylene-vinyl acetate-acrylic terpolymers, and urethane polymers. The polymers may contain up to 10% by weight of functional monomers, (for example, but not limited to, carboxylic acid, phosphate, sulfate, sulfonate and amide) groups, other monomers, and mixtures thereof. Latex polymeric binders optionally incorporated in prepaints x, y, x', y', or other prepaints may be the same as or different from the latex polymeric binder of prepaint z.

It is conceivable that for industrial coatings the prepaints will employ a wide range of thermoplastic and thermosetting polymeric binders, that may be one-pot, two-pot or energy-curable, in the prepaints and methods of the inventions, including but not limited to: asphalt, paraffin wax, coal tar, alkyds, vinyl acetate, vinyl acetate/acrylic, styrene-butadiene, saturated polyester, unsaturated polyester, polyurethane, acrylic lacquer, acrylic enamel, acrylic latex, acrylic thermosetting, acrylic electrodeposition and autodeposition, styrene acrylic, vinyl toluene acrylic, radiation-curable acrylic, melamine, urea, epoxy (diglycidyl ether of bisphenol A, bisphenol F, cycloaliphatic, monofunctional epoxies and the like), vinyl acetate copolymer N-methylolacrylamide, vinyl acetate-ethylene, vinyl acetate terpolymer, vinyl acetate-vinyl versatate, polyvinyl chloride, polyvinylidene chloride, ethylene-acrylic acid, ethylene-methacrylic acid, ionomer, ethylene-

methyl acrylate, cellulosics, nitrocellulose, cellulose acetate butyrate, shellac, phenolic, ethyl silicate, polyacetals, styrene-allyl alcohol, chlorinated rubber, polyvinyl alcohol, butyl rubber, styrene—ethylene butylenes—styrene block copolymer rubber, urethane acrylate, polyamideimide, polyesterimide, silicones, silanes, shellac, polyamides, polytetrafluoroethylene, polydiallyldimethylammonium chloride, polyphenylene sulfide, aromatic polyester, polyimide, siliconeimide, fluoropolymers, parylene, aramid, stelarate polymers, oleoresinous, and chlorinated polyolefin and bis-cyclobenzobutene. The polymeric binders are preferably water-borne latexes, but may also be solvent-borne, water reducible, redispersible latexes, and combinations thereof.

Emphasis was added to identify particularly important terms for use in later discussion.

### **III. SUMMARY OF REASONS FOR REEXAMINATION**

Claim 1 of the '537 patent, Exhibit A, recites:

1. A set of different, but mutually compatible fluid prepaints, sufficient to form at least one paint line, which set comprises:
  - i) at least one opacifying prepaint comprising at least one opacifying pigment;
  - ii) at least one extender prepaint comprising at least one extender pigment; and
  - iii) at least one binder prepaint comprising at least one latex polymeric binder.

The remaining claims either expand upon this claim theme or take a particular component from this basic claim, such as the opacifying pigment, the extender pigment and the polymeric binder, and define it in more specific terms.

The Friel '537 patent claims are invalid because each element of every claim of the '537 patent is anticipated by or made obvious by the disclosure of McClain, Brock, Heuwinkel and other various prior art references taken alone or in combination.

Substantial new questions of patentability that were not addressed during prosecution of the '537 patent are raised by the disclosures of McClain, Brock and Heuwinkel each expressly disclosing every element of the broadest claims of the '537 patent. One substantial new question of patentability is further emphasized by Rohm & Haas' law suit asserting that a system similar to that disclosed in the McClain patent infringes the '537 patent. If the McClain patent was fully considered by the Office as prior art to the '537 patent, but a system built in accordance with the McClain disclosure infringes a claim of the '537 patent, the '537 patent is invalid and must be reexamined. Additionally, because all of the elements of the claims of the '537 patent are disclosed, taught or suggested by the references as discussed below, the '537 patent claims are invalid and must be reexamined.

#### **IV. APPLICATION OF THE UNAPPLIED PRIOR ART RAISES SIGNIFICANT NEW QUESTIONS OF PATENTABILITY**

Although McClain, Brock and Heuwinkel are cited on the face of the '537 patent, they were not applied during prosecution. In fact, no prior art was applied during prosecution. Rohm & Haas' own pending application that included identical claims was cited as a provisional rejection but was dropped when Rohm & Haas canceled the claims of that other application. "The existence of a substantial new question of patentability is not precluded by the fact that a patent or printed publication was previously cited by or to the Office or considered by the Office." 35 USCS § 303(a) (2004).

As shown more fully below, application of the unapplied prior art references raises significant new questions of patentability because the claims of the '537 patent are

anticipated and made obvious by numerous unapplied references. Each of the references to McClain, Brock and Heuwinkel will be separately applied to the primary '537 patent claims first, followed by a claims chart that details how each of the elements of the remaining claims is shown or described in the prior art or made obvious by the prior art.

Many of the '537 patent claims recite that the components are "mutually compatible" or "compatible" without stating to what degree of compatibility is required. The '537 patent defines "mutually compatible" by stating that prepaints are considered "mutually compatible if the paints formed by admixing the prepaints do not evidence signs of colloidal instability such as flocculation." Colloidal instability includes flocculation among other undesirable paint characteristics such as settling. Paint manufacturers long ago learned to overcome the problems of instability, settling, and flocculation through adjustments to the pH levels and chemicals used to form the paint and by adding additional components to the paint such as a dispersant. *See Coatings Encyclopedic Dictionary*, 1995, edited by Stanley LeSota (hereinafter "Coatings Dictionary"), "flocculation", p. 118 at Exhibit B; *see also* Tsuei (U.S. Patent 5,643,669), col. 6, lines 20-26 explaining the well known meaning of "compatible". The '537 patent specification asserts that there is **no sign** of colloidal instability. The claims use the broad term "mutually compatible" which, given its broadest possible interpretation, could be broadly interpreted to include the situation where the prepaints mix initially without immediate flocculation, but separate over time. The claims do not indicate to what level the components are compatible or whether any particular level of mutual compatibility is

necessary to infringe. Taking the language in its broadest possible interpretation, it will be initially presumed that the level of mutual compatibility referred to in the '537 patent claims is in accordance with that of conventional paint components used to form conventional paint having colloidal stability and that there is no particular novelty to this component of the claim.

**A. The Unapplied McClain Patent Discloses an Opacifying Prepaint, an Extender Prepaint and a Binder Prepaint.**

McClain relates to a system of non-paint aqueous compositions which when mixed together form paint. *See* McClain Abstract. The "pre-paints" of McClain are "pre-paints" because they are aqueous compositions that are not paints prior to being mixed and form paint when mixed.

McClain discloses among its four pre-paints a Pigment Composition that includes the pigment titanium dioxide. *See* McClain at col. 2, lines 25-28, Exhibit C. Titanium dioxide is expressly identified in the '537 patent as a suitable opacifying pigment. *See* '537 patent, col. 10, lines 8-25, Exhibit A. Therefore, McClain discloses a pigment prepaint comprising an opacifying pigment.

McClain discloses among its four pre-paints a Low Resin Composition that includes approximately 11 percent ground limestone. *See* McClain at col. 3, lines 33-34, Exhibit C. Ground limestone is commonly called "natural calcium carbonate". *See* Coatings Dictionary at pp. 49 and 166, Exhibit B. Calcium carbonate is expressly identified in the '537 patent as a suitable extender pigment. *See* '537 patent, col. 10, line

53 to col. 11, line 2, Exhibit A. Therefore, McClain discloses an extender prepaint comprising an extender pigment.

McClain discloses among its four pre-paints a High Resin Composition that includes approximately 80 percent resin and gives an example of 6183 BASF resin but states that other commercially available resins can be used if desired. *See* McClain at col. 3, lines 39-48, Exhibit C. The product 6183 BASF has been renamed by BASF since the McClain patent was filed to Acronal Optive 220 (also called Acronal TM DS 6183). A product description is included as Exhibit T, hereto. 6183 BASF is a well known polymer acrylic resin binder that is commonly used to make latex paints. Acrylic polymers are expressly identified in the '537 patent as a suitable latex polymeric binder. *See* '537 patent, col. 11, lines 3-59, Exhibit A. Therefore, McClain discloses a binder prepaint comprising a latex polymeric binder.

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McClain's Pigment Composition, Low Resin Composition and High Resin Composition each anticipate the '537 patent's pigment prepaint, extender prepaint and binder prepaint, respectively. These are the only three elements of the '537 patent's claim 1. Because every element of independent claim 1 of the '537 patent is disclosed by McClain, McClain anticipates claim 1. Additionally, McClain teaches a method of mixing the prepaints together in varying proportions dispensed into containers to form a paint line and, thus, also anticipates claim 5 of the '537 patent. *See* McClain, col. 3, lines 49-55. Claim 6 of the '537 patent is anticipated or at least made obvious by the teachings of McClain to provide alternative mixtures of the prepaint components with different

amounts of resin and water in the low and high resin compositions to achieve different paint characteristics (or paint lines). *See McClain, col. 3, lines 40-54.*

The specifics of all of the '537 patent claims are addressed in the claim charts, provided later in this Request.

**B. The Unapplied Brock Patent Discloses an Opacifying Prepaint, an Extender Prepaint and a Binder Prepaint.**

Brock relates to a system of non-paint aqueous coating modules which when mixed together form a lacquer. *See Brock Abstract, Exhibit D.* The '537 patent defines "paint" as a "term used in its broadest sense and includes any coating that may be applied to a surface for decorative, protective or both purposes." *See '537 patent col. 3, line 66 to col. 4, line 1, Exhibit A.* The Coatings Dictionary, p. 203 at Exhibit B, more narrowly defines the noun paint as "[a]ny pigmented liquid, liquefiable, or mastic composition designed for application to a substrate as a thin layer which is converted to an opaque solid film after application." "Lacquer" is a pigmented liquid used to coat surfaces that hardens to a solid film. All lacquer is, therefore, "paint" within the definition of paint in the '537 patent, and all but clear lacquer is paint under a conventional definition of paint. The lacquer modules of Brock are "pre-paints" because they are aqueous compositions that are not paints prior to being mixed and form a decorative and/or protective coating when mixed.

Brock discloses among its pre-paint modules both Special Effect Modules and Dye Modules that each include opacifying pigments. The Special Effect Modules

include one or more of titanium dioxide coated pigments, titanium dioxide coated aluminum or titanium dioxide coated mica. *See Brock, col. 2, lines 54-63, Exhibit D.* The Dye Modules include one or more of titanium dioxide, micronised titanium dioxide, iron oxide pigments and silicon dioxide, among other options. *See Brock, col. 7, lines 34-47, Exhibit D.* Titanium dioxide is expressly identified in the '537 patent as a suitable opacifying pigment. *See '537 patent, col. 10, lines 8-25, Exhibit A.* Therefore, Brock discloses at least two prepaint modules that are opacifying prepaints comprising an opacifying pigment.

Brock discloses among its pre-paint modules Dye Modules and Rheology Modules that each include extender pigments. The Dye Modules include one or more of barium sulfate and micronised mica, among other options. *See Brock, col. 7, lines 34-47, Exhibit D.* The Rheology Modules include one or more of aluminum magnesium silicate and sodium magnesium sheet silicate, among other options. *See Brock, col. 8, lines 14-26, Exhibit D.* Barium sulfate, mica, silica, magnesium silicate, aluminum silicate and magnesium alumino-silicate are expressly identified in the '537 patent as suitable extender pigments. *See '537 patent, col. 10, line 53 to col. 11, line 2.* Therefore, Brock discloses at least two prepaint modules that are extender prepaints comprising an extender pigment.

Brock discloses among its pre-paint modules Special Effects Modules, Binder Modules, Dye Modules, Rheology Modules and Cross-Linking Modules that each include latex polymeric binders. The Special Effects Modules, Binder Modules, Dye

Modules and Cross-Linking Modules each include water-dilutable resins that are conventional film-forming binders based upon polyesters, polyacrylates or polyurethanes, specifically including acrylic and methacrylic copolymers. *See Brock, col. 3, lines 20-38, col. 4, lines 14-45, col. 7, lines 34-38 and 48-56, col. 9, lines 12-17, Exhibit D.*

Additionally, the Rheology Modules include polymeric microparticles such as synthetic polymers and polyurethane. *See Brock, col. 8, lines 14-26, Exhibit D.* Acrylic and methacrylic copolymers, urethane polymers as well as many other synthetic polymers are expressly identified in the '537 patent as suitable latex polymeric binders. *See '537 patent, col. 10, line 53 to col. 11, line 2.* Therefore, Brock discloses at least five prepaint modules that are binder prepaints comprising a latex polymeric binder.

Brock's prepaint modules anticipate the '537 patent's pigment prepaint, extender prepaint and binder prepaint as shown above. These are the only three elements of the '537 patent's claim 1. Because every element of independent claim 1 of the '537 patent is disclosed by Brock, Brock anticipates claim 1. Additionally, Brock teaches a method of mixing various prepaints together in varying proportions dispensed into containers to form a paint line and, thus, also anticipates claim 5 of the '537 patent. *See Brock, col. 11, line 64 to col. 12, line 13.* Claim 6 of the '537 patent is also anticipated by Brock in that Brock provides additional different modules meeting the elements of one or more of a pigment prepaint, extender prepaint and binder prepaint that when combined with the previous prepaints provide alternate characteristics to the paint formed to create at least a

second paint line. *See* Brock, col. 10, line 19 to col. 12, line 13. The specifics of all of the '537 patent claims are addressed in the claim charts provided later in this Request.

**C. The Unapplied Heuwinkel Patent Discloses an Opacifying Prepaint, an Extender Prepaint and a Binder Prepaint.**

Heuwinkel relates to a modular system and process for producing aqueous coating compositions from non-paint aqueous modules which when mixed together form a lacquer. *See* Heuwinkel Abstract, Exhibit E. The '537 patent defines "paint" as a "term used in its broadest sense and includes any coating that may be applied to a surface for decorative, protective or both purposes." *See* '537 patent col. 3, line 66 to col. 4, line 1, Exhibit A. Lacquer is, therefore, within the scope of the term "paint" of the '537 patent. The "pre-paint" modules of Heuwinkel are "pre-paints" because they are aqueous compositions that are not paints prior to being mixed and form a decorative and/or protective coating when mixed.

Heuwinkel discloses among its pre-paint modules both Effect Modules and Colour Modules that each include opacifying pigments. The Effect Modules include one or more of titanium dioxide coated aluminum or titanium dioxide coated mica. *See* Heuwinkel, p.18, lines 18-23, Exhibit E. The Colour Modules include one or more of titanium dioxide, micronised titanium dioxide, iron oxide pigments and silicon dioxide, among other options. *See* Heuwinkel, p. 15, lines 21-32, Exhibit E. Titanium dioxide is expressly identified in the '537 patent as a suitable opacifying pigment. *See* '537 patent, col. 10, lines 8-25, Exhibit A. Therefore, Heuwinkel discloses at least two prepaint modules that are opacifying prepaints comprising an opacifying pigment.

Heuwinkel discloses among its pre-paint modules Colour Modules and Rheology Modules that each include extender pigments. The Colour Modules include one or more of barium sulfate and micronised mica, among other options. *See Heuwinkel, p. 15, lines 21-32, Exhibit E.* The Rheology Modules include one or more of aluminum magnesium silicate and sodium magnesium phyllosilicate, among other options. *See Heuwinkel, p. 25, line 32 to p. 26, line 11, Exhibit E.* Barium sulfate, mica, silica, magnesium silicate, aluminum silicate and magnesium alumino-silicate are expressly identified in the '537 patent as suitable extender pigments. *See '537 patent, col. 10, line 53 to col. 11, line 2.* Therefore, Heuwinkel discloses at least two prepaint modules that are extender prepaints comprising an extender pigment.

Heuwinkel discloses among its pre-paint modules Effects Modules, Binder Modules, Colour Modules and Rheology Modules that each include latex polymeric binders. The Effects Modules, Binder Modules and Colour Modules each include water-dilutable resins that are conventional film-forming binders based upon polyesters, polyacrylates or polyurethanes, specifically including acrylic and methacrylic copolymers. *See Heuwinkel, p. 6, line 26 to p. 7, line 15, p. 15, line 34 to p. 17, line 36, and p. 18, lines 9-16, Exhibit E.* Additionally, the Rheology Modules include polymeric microparticles such as synthetic polymers and polyurethane. *See Heuwinkel, p. 25, line 32 to p. 26, line 15, Exhibit E.* Acrylic and methacrylic copolymers, urethane polymers as well as many other synthetic polymers are expressly identified in the '537 patent as suitable latex polymeric binders. *See '537 patent, col. 10, line 53 to col. 11, line 2.*

Therefore, Heuwinkel discloses at least four prepaint modules that are binder prepaints comprising a latex polymeric binder.

Heuwinkel's prepaint modules anticipate the '537 patent's pigment prepaint, extender prepaint and binder prepaint as shown above. These are the only three elements of the '537 patent's claim 1. Because every element of independent claim 1 of the '537 patent is disclosed by Heuwinkel, Heuwinkel anticipates claim 1. Additionally, Heuwinkel teaches a method of mixing various prepaints together in varying proportions dispensed into containers to form a paint line and, thus, also anticipates claim 5 of the '537 patent. *See* Heuwinkel, p. 1, lines 6-27. Claim 6 of the '537 patent is also anticipated by Heuwinkel in that Heuwinkel provides additional different modules meeting the elements of one or more of a pigment prepaint, extender prepaint and binder prepaint that when combined with the previous prepaints provide alternate characteristics to the paint formed to create at least a second paint line. *See* Heuwinkel, pp. 32-43. The specifics of all of the '537 patent claims are addressed in the claim charts provided later in this Request.

**D. Claims Chart: The Unapplied References Anticipate and Make Obvious the Claims of the '537 Patent – Raising Significant Questions of Patentability**

The claims chart provided below set forth the claims of the '537 patent with an explanation showing how the claims are *prima facie* anticipated or obvious in view of the various prior art references. The prior art references relied upon in the claim chart are found in the Attachments hereto, Exhibits C-S. Patents/Applications by Named Inventor:

<u>First Inventor</u>	<u>Attachment</u>	<u>Reference Number</u>
McClain	Exhibit C	US 6,221,145
Brock	Exhibit D	US 5,672,649
Heuwinkel	Exhibit E	CA 2,166,290
Falcoff	Exhibit F	US 4,403,866
Brown	Exhibit G	US 5,521,234
Kitano	Exhibit H	US 4,436,845
Sperry	Exhibit I	US 4,243,430
Kowalski	Exhibit J	US 4,880,842
Bauer	Exhibit K	US 5,989,331
Pyves	Exhibit L	CA 935,255
Landy	Exhibit M	US 5,527,853
Tsuei	Exhibit N	US 5,643,669

Other Articles referenced later by portions of titles:

<u>Title Portion</u>	<u>Attachment</u>
Form Postponement	Exhibit O
Component Mixing	Exhibit P
Delayed Product Differentiation	Exhibit Q
Batch Processes	Exhibit R
Paint Production	Exhibit S

## CLAIMS CHARTS

U.S. Patent No. 6,531,537	Prior Art References
1. A set of different, but mutually compatible fluid prepaints, sufficient to form at least one paint line, which set comprises:	<p>Each of McClain (col. 1, lines 47-50), Brock (col. 2, lines 1-45) and Heuwinkel (p. 3, line 1 to p. 5, line 19) discloses a set of fluid prepaints sufficient to form a paint line when mixed in varying amounts.</p> <p>McClain (col. 3, lines 49-51 – no settling), Brock (col. 2, lines 36-40 – storage-stable), and Heuwinkel (page 5, lines 1-4 – storage-stable) each disclose stable, mutually compatible prepaints. Settling is one form of colloidal instability (criteria for mutually compatible established by '537 patent at col. 4, lines 7-9). The prepaints of McClain, Brock, and Heuwinkel are mutually compatible because they are stable and form usable paint after mixing. No specific level of "mutually compatible" is described or claimed.</p>
(i.) at least one opacifying prepaint comprising at least one opacifying pigment;	Each of McClain (col. 2, lines 25-28; Pigment Composition), Brock (col. 2, lines 54-63 and col. 7, lines 34-47; Special Effect and Dye Modules), and Heuwinkel (p. 18, lines 18-23 and p. 15, lines 21-32; Effect and Colour Modules) discloses titanium dioxide as a component of at least one of its prepaints. The '537 patent expressly lists titanium dioxide as a suitable opacifying pigment.
(ii.) at least one extender prepaint comprising at least one extender pigment; and	<p>McClain (col. 3, lines 33-34; Low Resin Composition) discloses a prepaint comprising approximately 11 percent ground limestone. Ground limestone is natural calcium carbonate. The '537 patent expressly discloses calcium carbonate as a suitable extender pigment.</p> <p>Each of Brock (col. 7, lines 34-47 and col. 8, lines 14-26; Dye and Rheology Modules) and Heuwinkel (p. 15, lines 21-32 and p. 25, line 32 to p. 26, line 11; Colour and Rheology Modules) discloses at least two distinct prepaints each comprising at least one component expressly identified in the '537 patent as a suitable extender pigment.</p>

U.S. Patent No. 6,531,537	Prior Art References
(iii.) at least one binder prepaint comprising at least one latex polymeric binder.	<p>McClain (col. 3, lines 39-48; Low and High Resin Compositions) discloses at least two prepaints that comprise a latex polymeric binder as disclosed in the '537 patent.</p> <p>Each of Brock (col. 3, lines 20-38, col. 4, lines 14-45, col. 7, lines 34-38 and 48-56, col. 8, lines 14-26 and col. 9, lines 12-17; Special Effects, Binder, Dye, Rheology and Cross-Linking Modules) and Heuwinkel (p. 6, line 26 to p. 7, line 15, p. 10, line 53 to col. 11, line 2, p. 15, line 34 to p. 17, line 36, p. 18, lines 9-16 and p. 25, line 32 to p. 26, line 15; Effects, Binder, Colour and Rheology Modules) discloses many distinct prepaints that comprise a latex polymeric binder (conventional film-forming binders such as (meth)acrylic copolymers, urethane polymers, polyesters, polyurethanes, associative thickeners based on polyurethane or cellulose, synthetic polymers such as poly (meth)acrylic acid) as disclosed in the '537 patent.</p>

U.S. Patent No. 6,531,537	Prior Art References
2. The set of prepaints of claim 1, wherein the number of prepaints is from 3 to 15.	<p>Brock (col. 10, line 19 to col. 12, line 13) discloses at least six specific distinct prepaints, two each of a binder module, a special effect module and a dye module. Brock (col. 3, lines 55-61, col. 6, line 64 to col. 7, line 3, col. 7, lines 57-67, col. 9, lines 12-31) also teaches that rheology modules and cross-linking modules, as well as additional other modules may be added to the existing modules or separately as independent modules leaving a very large number of possible prepaints within the set.</p> <p>The disclosure of Heuwinkel is similar to, but more detailed than Brock and specifically discloses fourteen distinct prepaints, namely four binder modules, two effect modules, a rheological module, three colour modules and four crosslinking modules (pp. 38-43), that can be used in various combinations to form paint lines with different paint characteristics.</p> <p>McClain (col. 4, lines 5-12) discloses at least four individual prepaints within the set, and teaches that low and high resin compositions with different amounts of resin and water (which would necessarily involve additional prepaints) will result in different finish characteristics. Further, Falcoff teaches to form paint using at least six different solutions. It would have been obvious from the disclosure of McClain alone, but particularly in combination with the teachings of Falcoff, Brock and Heuwinkel to increase the number of prepaints in the system of McClain to thereby increase the variety of paint characteristics available from mixing prepaints. It would also be obvious from the disclosure of McClain to utilize additional prepaint compositions, such as known paint additives, to vary the quality, special effects, color, and other finish characteristics of the paint lines formed from the prepaints.</p>
3. The set of prepaints of claim 1, wherein the opacifying prepaint further comprises at least one particulate polymeric binder adsorbed onto the opacifying pigment.	Both Brock (col. 2, line 49 to col. 4, line 6 and col. 7, line 36 to col. 8, line 13 ) and Heuwinkel (page 15, line 12 to page 20, line 9 ) disclose particulate polymeric binders within the opacifying prepaint. It is inherent that the particulate polymeric binder would adsorb onto the opacifying pigment within the opacifying prepaint.

U.S. Patent No. 6,531,537	Prior Art References
4. The set of prepaints of claim 1, wherein the extender prepaint further comprises at least one particulate polymeric binder absorbed onto the extender pigment.	Both Brock (col. 2, line 49 to col. 4, line 6 and col. 7, line 36 to col. 8, line 13) and Heuwinkel (page 15, line 12 to page 20, line 9) disclose particulate polymeric binders within the extender prepaint. Furthermore, McClain (col. 3, lines 33-34) discloses a particulate polymeric binder within the extender prepaint. It is inherent that the particulate polymeric binder would absorb onto the extender pigment within the extender prepaint.
5. A method of forming at least one paint line, comprising the steps of:	Each of McClain (col. 1, lines 46-48, col. 3, lines 40-44 and col. 4, lines 1-13), Brock (col. 2, lines 1-45) and Heuwinkel (p. 3, line 1 to p. 5, line 19) discloses a method of forming at least one paint line involving steps.
(a) providing a set of different, but mutually compatible, fluid prepaints, comprising:	See claim 1.
(i) at least one opacifying prepaint, comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment; and	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymeric binder; and	See claim 1(iii).
(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the paint line.	McClain (col. 1, lines 46-48, col. 3, lines 40-54 and col. 4, lines 1-13), Brock (col. 2, lines 1-45) and Heuwinkel (p. 3, line 1 to p. 5, line 19) each disclose dispensing the prepaints to form paint. The prepaints are necessarily dispensed into a container or applicator to enable mixing of the paint to form the paint line.  Furthermore, Falcoff (col. 5, lines 7-9) discloses dispensing solutions into a mixing container and then into suitable containers. To whatever extent it is not expressly disclosed in Brock and Heuwinkel, it would have been obvious to dispense the prepaints into a suitable container for use from the disclosures of McClain and Falcoff.

U.S. Patent No. 6,531,537	Prior Art References
6. A method of forming a range of paints, the range comprising at least two paint lines, which method comprises the steps of:	Each of McClain (col. 1, lines 46-48, col. 3, lines 40-54 and col. 4, lines 1-13), Brock (col. 2, lines 1-45) and Heuwinkel (p. 3, line 1 to p. 5, line 19) discloses a method of forming at least two paint lines involving steps.
(a) providing a set of different, but mutually compatible, fluid prepaints sufficient to formulate at least two paint lines, which set comprises:	See claim 1.  Brock (col. 12, lines 1-13 at cols. A and B) and Heuwinkel (pp. 42-43) each discloses at least two paint lines.  McClain expressly discloses a first paint line at col. 4, lines 1-13, and discloses at least a second paint line at col. 3, lines 40-44 by teaching that the high and low resin compositions may be made with different amounts of resin and water to result in different finish characteristics (i.e. a different paint line).
(i) at least one opacifying prepaint, comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment;	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymeric binder; and	See claim 1(iii).

U.S. Patent No. 6,531,537	Prior Art References
(iv) at least one additional, different opacifying, extender, or binder prepaint selected from the group consisting of (i), (ii), and (iii); and	<p>Brock's Special Effect Modules each qualify as opacifying prepaints, its Dye Modules qualify as extender pigments, and its Binder Modules qualify as binder prepaints (in addition to each module qualifying under other categories of prepaints). Brock (col. 10, line 19 to col. 12, line 13) expressly discloses two different binder modules, two different special effect modules and two different dye modules. The additional, different prepaint modules of Brock also qualify as different opacifying, extender and binder prepaints selected from the group consisting of (i), (ii), and (iii).</p>
	<p>Heuwinkel's Effect Modules each qualify as opacifying prepaints, its Colour Modules qualify as extender pigments, and its Binder Modules qualify as binder prepaints (in addition to each module qualifying under other categories of prepaints). Heuwinkel specifically discloses three colour modules, two effect modules and four binder modules (pp. 38-43). The additional, different prepaint modules of Heuwinkel also qualify as different opacifying, extender and binder prepaints selected from the group consisting of (i), (ii), and (iii).</p>
	<p>In addition to McClain's Pigment Composition, Low Resin Composition and High Resin Composition that each qualify as an opacifying prepaint, an extender prepaint and a binder prepaint, respectively, McClain (col. 3, lines 40-54) further teaches that the use of low and high resin compositions with different amounts of resin and water will result in different finish characteristics. This inherently involves at least one additional extender prepaint and/or binder prepaint from (ii) and (iii).</p>
	<p>Further, Falcoff (FIG. 1 and col. 3, lines 49-54) teaches to form paint using at least six different prepaint solutions (binder solution, two pigment dispersions, and three tinting solutions). It would have been obvious from the disclosure of McClain alone, but particularly in combination with the teachings of Falcoff, Brock or Heuwinkel, to provide a different opacifying, extender or binder prepaint in addition to the other prepaints provided to thereby increase the variety of paint characteristics (or paint lines) that can result from forming paint from prepaints.</p>

U.S. Patent No. 6,531,537	Prior Art References
(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the range of paints.	See Claim 5(b).
7. The method of claim 5, further comprising the step of mixing the prepaint before, while, or after they are dispensed into the containers.	The use of "before, while, or after" is considered non-limiting. Nevertheless, McClain (col. 3, lines 6-8, 25-29 and 50-54), Brock (col. 9, lines 18-40), Heuwinkel (page 27, lines 5-29, page 28, lines 11-22, and page 29, lines 22-27) and Falcoff (FIG. 1 and col. 3, lines 55-65 and col. 5, lines 7-9) each disclose mixing the prepaints before, while and after dispensing into containers. Furthermore, it is well known to shake or stir cans of paint "after" paint is dispensed into them, the prepaints necessarily mix "while" dispensing into either a mixing container or the final container or applicator, and it would be obvious to pour the prepaints into a mixing container for mixing "before" later dispensing the paint to a final container or applicator.
8. The method of claim 5, further comprising the step of mixing the prepaint before or while they are dispensed into the applicator(s).	See claim 7. The '537 patent does not give any details as to what an "applicator" is. Accordingly, it is noted that a container could also be an applicator or additionally it would have been obvious to provide applicators as the containers to remove the need to transfer the paint or prepaints from the container to a separate applicator.
9. The method of claim 5, further comprising the step of adjusting the viscosity of the prepaints before, while, or after they are dispensed into the containers.	The use of "before, while, or after" is considered non-limiting. Nevertheless, McClain (col. 2, lines 36-38, 50-54 and 59-60 and col. 3, lines 6-8, 16-17 – viscosity controlling agent and thickeners), Brock (col. 2, lines 37-40, col. 3, lines 59-61 and col. 9, lines 32-40 – viscosity components, thickeners and water), Heuwinkel (page 28, lines 11-22 and page 29, lines 22-27 – viscosity components, thickeners and water) and Brown (col. 1, lines 34-43 and col. 2, lines 43-55), each disclose adjusting the viscosity of prepaints before, while and after dispensing. Additionally, it is well known in the paint art to add viscosity controlling or rheology modifying agents to paints.

U.S. Patent No. 6,531,537	Prior Art References
10. The method of claim 5, further comprising the step of adjusting the viscosity of the dispensed prepaints before or while they are dispensed into the applicator(s).	See claims 7, 8 and 9.
11. The method of claim 5, further comprising the step of adding at least one additive that enhances application or final performance of the paint.	The use of additives to paint is well known in the paint art and all of the references cited herein are replete with examples of additives that enhance application or final performance of paint. <i>See Coatings Dictionary</i> , pp. 7 and 348-349, Exhibit B. McClain (col. 2, line 40 and 59-60, col. 2, line 67 to col. 3, line 3, col. 3, lines 16-17 and 34-37), Brock (col. 3, lines 62-64), Heuwinkel (page 28, lines 11-22) and Falcoff (FIG. 1 and col. 3, line to col. 5, line 9) expressly disclose additives for paint.
12. The method of claim 11, wherein the additive is on aggregate material.	Aggregate is a well known additive for paint. <i>See</i> Kitano, col. 3, lines 27-35 (glass beads fall under the definition of an aggregate within the '537 patent). It would have been obvious from the disclosures of any of McClain, Brock or Heuwinkel in light of Kitano to include aggregate as an additive to the paint or any prepaint. <i>See also</i> , Tsuei (col. 9, lines 43-65, col. 10, lines 24-48, and col. 16, lines 39-64).
13. The method of claim 11, wherein the additive is a thickener.	The use of thickeners as additives to paint is well known in the art. McClain (col. 2, lines 59-60 and col. 3, lines 16 – 17), Brock (col. 2, lines 37-40, col. 3, lines 59-61 and col. 9, lines 32-40), and Heuwinkel (page 28, lines 11-22) each disclose adding thickeners to paint and/or one or more prepaints.
14. The method of claim 5, further comprising the step of adding at least one colorant to the prepaints.	The '537 appears to use the term "colorant" in its ordinary meaning and does not define "colorant" by its use. The Coatings Dictionary, p. 73 defines a colorant as: "any substance that imparts color." <i>See</i> Exhibit B. It was well known in the art at the time of the '537 patent invention to add color to paint. Furthermore, McClain (col. 3, lines 55-56), Brock (col. 7, lines 34-47 and col. 11, lines 35 and 54), Heuwinkel and Falcoff (FIG. 1 and col. 3, line to col. 5, line 9) each recite the addition of colorant to prepaints.

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15. The method of claim 5, wherein the opacifying prepaint further comprises at least one particulate polymeric binder absorbed onto the opacifying pigment.	See claim 3.
16. The method of claim 5, wherein the extender prepaint further comprises at least one particulate polymeric binder absorbed onto the extender pigment.	See claim 4.
17. The method of claim 5, wherein the method is carried out at a paint manufacturing facility.	Paint manufacturing is inherently carried out at a paint manufacturing facility (wherever it may be located). Furthermore, McClain (col. 1, lines 23-25) and Falcoff (col. 2, lines 39-42 and col. 5, lines 23-25) each disclose making paint in a central (e.g., manufacturing) facility.
18. The method of claim 5, wherein the number of prepaints is from 4 to 15.	See claim 2.
19. A fluid opacifying prepaint useful for formulating a one pack, pigmented latex paint having a volume solids content of about 30% to about 70% and	<p>See claim 1(i) and 1(iii). Additionally, Tsuei (col. 3, lines 14-31, col. 4, lines 2-21, col. 6, lines 16-32, col. 7, lines 15-47, col. 9, lines 44-65 and col. 16, lines 39-64) discloses a fluid opacifying prepaint for a pigmented latex paint.</p> <p>Brock (col. 9, lines 42-43) discloses that its pigmented latex paint includes a volume solids content of 10% to 40%.</p> <p>Heuwinkel (page 6, lines 21-23) discloses that its pigmented latex paint includes a volume solids content of 10%-80%.</p> <p>Tsuei (col. 3, lines 14-31) discloses that its pigmented latex paint includes a solids content by weight of about 30%-70%.</p>

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a Stormer viscosity of about 50 to about 250 KU, which prepaint contains other paint ingredients, which prepaint consists essentially of:	It is inherent that the Stormer viscosity of the pigmented latex paint of McClain, Brock, Heuwinkel and Tsuei is between about 50 to about 250 KU or would be obvious to adjust the composition to have a viscosity within that range by altering the quantity of thickening agent added until the desired viscosity is achieved. Additionally, Brown specifically discloses a Stormer viscosity of 85-95 KU. Specific ranges of Stormer viscosity would have been obvious.
(i) at least one opacifying pigment,	See claim 1(i). See also, Tsuei (col. 7, lines 15-36, col. 9, lines 44-65 and col. 16, lines 39-64).
(ii) at least one dispersant,	Each of McClain (col. 2, lines 43-51), Brock (col. 2, line 49 to col. 4, line 13 and col. 7, line 36 to col. 8, line 13 – special effects module and dye module), Heuwinkel (page 15, line 12 to page 20, line 9 – effect module and colour module) discloses adding dispersant to an opacifying prepaint, and Tsuei (col. 4, lines 2-21 and col. 6, lines 16-32).
(iii) at least one thickener, and	Each of McClain (col. 2, lines 31-32), Brock (col. 2, line 49 to col. 4, line 13 and col. 7, line 36 to col. 8, line 13 – special effects module and dye module), Heuwinkel (page 15, line 12 to page 20, line 9 – effect module and colour module) discloses adding thickener to an opacifying prepaint, and Tsuei (col. 6, lines 16-54).
(iv) water;	Each of McClain (col. 2, lines 57-60), Brock (col. 2, line 49 to col. 4, line 13 and col. 7, line 36 to col. 8, line 13 – special effects module and dye module), Heuwinkel (page 15, line 12 to page 20, line 9 – effect module and colour module) discloses adding water to an opacifying prepaint, and Tsuei col. 3, lines 14-31.
wherein the dispersant(s) and the thickener(s) are mutually compatible with the pigment(s) and with the other paint ingredients.	McClain (col. 3, lines 49-51 – no settling), Brock (col. 2, lines 36-40 – storage-stable), Heuwinkel (page 5, lines 1-4 – storage-stable), and Tsuei (col. 3, lines 14-31 and col. 6, lines 19-26) each disclose opacifying prepaints having dispersants, thickeners and pigments that are stable. Settling is one form of colloidal instability. The dispersants and the thickeners of McClain, Brock, and Heuwinkel are mutually compatible with the pigments because they are stable after mixing.

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20. The prepaint of claim 19 wherein the volume solids content is about 35% to about 50% and the Stormer viscosity is about 60 to about 150 KU.	See claim 19 relating to volume solids content and Stormer viscosity.
21. A fluid white opacifying prepaint	See claim 19. Titanium dioxide is a white opacifier.
having a volume solids content of about 30% to about 70%,  a PVC of about 35% to about 100%, and	Brock (col. 4, lines 9-10 – special effects module 10%-40% and col. 8, lines 9-10 – dye module 20%-80%), Heuwinkel (page 6, lines 14-15 -- colour module: 0%-60%; and effect module: 0%-50%) and Tsuei (col. 3, lines 14-31 – 30%-70%), each disclose white opacifying prepaints having a volume solids content of about 30% to about 70%. Specific ranges of volume solids content would have been obvious.
a Stormer viscosity of about 50 to about 250 KU,	Pigment volume concentration (PVC) for the opacifying prepaint within a specific range is either inherent or obvious from the cited references.
useful for formulating a one pack, pigmented latex paint containing other paint ingredients, which prepaint consists essentially of:	See claim 19.
(i) at least one opacifying pigment,	See claim 19(i).
(ii) at least one dispersant,	See claim 19(ii).
(iii) at least one thickener,	See claim 19(iii).
(iv) at least one film-forming or non-film-forming polymer, and	“Film-forming or non-film forming” polymer is considered non-limiting. McClain (col. 2, lines 36-38), Brock (col. 3, lines 33-38), Heuwinkel (col. 7, lines 48-55) and Tsuei (col. 3, lines 14-31) each disclose a polymer (film forming or non-film forming).

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(v) water; wherein the dispersant(s), the thickener(s), and the polymer(s) are compatible with the pigment(s) and with the other paint ingredients and wherein the prepaint is stable to sedimentation.	See claim 19(iv).
22. The prepaint of claim 21, wherein the volume solids content is about 35% to about 50%,	See claim 21.
the PVC is about 50 to about 100%, and	See claim 21.
the Stormer viscosity is about 60 to about 150 KU.	See claim 21.
23. The prepaint of claim 21, wherein the polymer is adsorbed onto the opacifying pigment.	See claims 3.
24. The prepaint of claim 19 or 21, wherein the opacifying pigment is a material selected from the group consisting of titanium dioxide, zinc oxide, lead oxide, a synthetic polymer pigment, and mixtures thereof.	See claim 1(i).  See also, Brown (col. 4, lines 9-36 – anatase and rutile TiO <sub>2</sub> and zinc oxide), Kitano (examples 1-6 – Rutile TiO <sub>2</sub> ), Sperry (col. 2, line 60 to col. 3, line 8 – TiO <sub>2</sub> , white lead, iron oxide, zinc oxide and “other reactive and unreactive pigments are well known in the art”), and Kowalski (Abstract and col. 1, lines 6-10 – voided synthetic polymer pigments).
25. The prepaint of claim 19 or 21, wherein the opacifying pigment is rutile titanium dioxide.	See claim 24. It would have been obvious to use rutile titanium dioxide in light of the referenced art.

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26. The prepaint of claim 24, wherein the synthetic polymer pigment is voided latex polymer particles.	See claim 24. It would have been obvious to use the voided synthetic polymer pigments of Kowolski in place of the pigments of McClain, Brock or Heuwinkel. Brock (col. 8, lines 14-26) discloses that its rheology module includes polymeric microparticles and/or synthetic polymers that are commercially obtainable in a variety of forms.
27. The prepaint of claim 19, wherein the dispersant is a selected from the group consisting of 2-amino-2-methyl-1-propanol; dimethylaminoethanol; potassium tripolyphosphate; trisodium polyphosphate; citric acid; polyacrylic acid; diolefin/maleic anhydride adducts; hydrophobically-modified polyacrylic acid, hydrophilically-modified polyacrylic acid, and salts thereof; and mixtures thereof.	McClain (col. 2, lines 43-47) discloses potassium tripolyphosphate as a dispersant for the opacifying prepaint. Bauer (col. 1, lines 61-65) discloses alkali polyphosphates, aliphatic carboxylic acids and salts thereof, polyacrylic acids and alkali salts thereof, polyhydroxy alcohols, and amino alcohols as dispersant components of a pigment slurry that would qualify as an opacifying prepaint under the '537 patent. Brock (col. 2, line 49 to col. 4, line 13 and col. 7, line 36 to col. 8, line 13) and Heuwinkel (page 15, line 12 to page 20, line 9) each disclose two opacifying prepaints having a dispersant. It would have been obvious to use one of the other well known dispersants available.
28. The prepaint of claim 19, wherein the thickener is a selected from the group consisting of an alkali-soluble or alkali-swellable emulsion (ASE), a hydrophobically-modified, alkali-soluble emulsion (HASE), a hydrophobically-modified ethylene oxide-urethane polymer (HEUR), a cellulosic, a hydrophobically-modified cellulosic, a hydrophobically-modified polyacrylamide, a polyvinyl alcohol, a fumed silica, an attapulgite clay, a titanate chelating agent, and mixtures thereof.	McClain (col. 2, lines 57-60) discloses cellulosic thickener in the opacifying prepaint. Pyves (pages 2 and 4) discloses cellulose derivative, polysaccharide gum, starches, polyvinyl alcohols, alginates, clay types, and acrylic types as thickener components of a pigment slurry that would qualify as an opacifying prepaint under the '537 patent. Brock (col. 3, lines 55-60, col. 7, lines 63-64, and col. 8, lines 14-26) and Heuwinkel (page 15, line 12 to page 20, line 9) each disclose two opacifying prepaints having a rheology regulating agent. It would have been obvious to use one of the other well known thickeners available.

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29. The prepaint of claim 21, wherein the polymer is selected from the group consisting of acrylic, polyvinyl acetate, styrene-acrylic, styrene-butadiene, vinyl acetate-acrylic, ethylene-vinyl acetate, vinyl acetate-vinyl versatate, vinyl acetate-vinyl maleate, vinyl acetate-vinyl chloride-acrylic, ethylene-vinyl acetate-acrylic polymers and mixtures thereof	See claim 1(iii). A review of the McClain, Brock and Heuwinkel sections listed in claim 1(iii) reveals many of these polymers listed here.
and wherein the polymer further comprises up to about 10% by weight of the polymer of a monomer selected from the group consisting of a functional monomer, a co-monomer, and combinations thereof.	Polymers inherently include a percentage by weight of the polymer of a monomer. A specific percentage would have been obvious or inherent in the specific polymer selected.
30. The prepaint of claim 19 or 21, further consisting essentially of at least one additive selected from the group consisting of an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide, and an antifreeze agent, with the additive being present in an amount of less than about 10% by weight, based on the total weight of the prepaint.	The use of additives to paint is well known in the paint art and all of the references relied upon with reference to claims 19 and 21 are replete with examples of paint additives. <i>See also</i> Coatings Dictionary, pp. 7 and 348-349, Exhibit B. McClain (col. 2, line 40 and 59-60, col. 2, line 67 to col. 3, line 3, col. 3, lines 16-17 and 34-37), Brock (col. 2, line 49 to col. 4, line 13 and col. 7, line 36 to col. 8, line 13), Heuwinkel (page 15, line 12 to page 20, line 9, and page 28, lines 11-22), Falcoff (FIG. 1 and col. 3, line 1 to col. 5, line 9), Pyves (pp. 2-5), Bauer (col. 1, lines 61-65) expressly disclose many of these additives for paint. A specific percentage by weight where the references do not restrict the amounts of additives and the variety of additives is so broad would have been obvious from the specific additive selected.
31. A fluid pigment extender prepaint, useful for formulating a one pack, pigmented latex paint containing other paint ingredients, which prepaint consists essentially of:	See claim 1(ii) and 1(iii).

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(i) at least one mineral extender having a volume solids content of about 30% to about 70%, a PVC of about 35% to about 100%, and a Stormer viscosity of about 50 to about 250 KU;	<p>The extender prepaint of McClain (col. 3, lines 33-34; Low Resin Composition) includes a mineral extender (ground limestone = calcium carbonate).</p> <p>Each of Brock (col. 2, line 49 to col. 4, line 13, col. 7, line 34 to col. 8, line 13, and col. 8, lines 14-26; Dye and Rheology Modules) and Heuwinkel (page 15, line 12 to page 20, line 9 and page 25, line 32 to page 27, line 4; Colour and Rheology Modules) discloses at least two distinct extender prepaints each comprising at least one mineral extender expressly identified in the '537 patent (mica, titanium dioxide, iron oxide, barium sulphate, silicates).</p> <p>Volume solids content, pigment volume concentration (PVC), and Stormer viscosity levels for the extender prepaint within a specific range that is typical of conventional paint is either inherent or obvious from the cited references for being typical of conventional paints.</p>
(ii) at least one thickener;	<p>Each of McClain (col. 3, line 35), Brock (col. 2, line 49 to col. 4, line 13, col. 7, line 34 to col. 8, line 13, and col. 8, lines 14-26 – special effects module, dye module and rheology module) and Heuwinkel (page 15, line 12 to page 20, line 9 and page 25, line 32 to page 27, line 4 – effect module, colour module and rheology module) (rheology regulating agents, such as polymeric microparticles, inorganic sheet silicates, associative thickeners based on cellulose, polyvinyl alcohols, synthetic polymers) discloses an extender prepaint with thickener.</p>
(iii) water, and	<p>McClain (col. 3, line 30) discloses that its extender prepaint is about 28 percent water. Brock (col. 2, line 49 to col. 4, line 13, col. 7, line 34 to col. 8, line 13, and col. 8, lines 14-26 – special effects module, dye module and rheology module) and Heuwinkel (page 15, line 12 to page 20, line 9 and page 25, line 32 to page 27, line 4 – effect module, colour module and rheology module), also disclose aqueous extender prepaints.</p>

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(iv) an optional polymeric binder;	<p>McClain (col. 3, line 30 and 44-46; Low Resin Compositions) discloses an extender pigment including about 50% polymeric binder.</p> <p>Each of Brock (col. 2, line 49 to col. 4, line 13, col. 7, line 34 to col. 8, line 13, and col. 8, lines 14-26 (the special effect module, the dye module, and the rheology module) and Heuwinkel (page 15, line 12 to page 20, line 9 and page 25, line 32 to page 27, line 4 (the colour module, the effect module, and the rheology module) discloses an extender pigment that includes a polymeric binder (conventional film-forming binders such as (meth)acrylic copolymers, urethane polymers, polyesters, polyurethanes, associative thickeners based on polyurethane or cellulose, synthetic polymers such as poly (meth)acrylic acid).</p>
wherein the prepaint ingredients are compatible with each other and with the ingredients of the paint.	See claim 1. McClain (col. 3, lines 49-51 – no settling), Brock (col. 2, lines 36-40 – storage-stable), and Heuwinkel (page 5, lines 1-4 – storage-stable) each disclose extender prepaints having compatible ingredients that are also compatible with the ingredients of the paint.
32. A set of two different, but mutually compatible binder prepaints useful for formulating a latex paint, which set comprises:	See claim 1(iii). Each of McClain (col. 3, lines 39-51; Low and High Resin Compositions), Brock (col. 2, lines 36-40, col. 3, lines 20-38, col. 4, lines 14-45, col. 7, lines 34-38 and 48-56, col. 8, lines 14-26 and col. 9, lines 12-17; Special Effects, Binder, Dye, Rheology and Cross-Linking Modules) and Heuwinkel (page 5, lines 1-4, p. 6, line 26 to p. 7, line 15, p. 10, line 53 to col. 11, line 2, p. 15, line 34 to p. 17, line 36, p. 18, lines 9-16 and p. 25, line 32 to p. 26, line 15; Effects, Binder, Colour and Rheology Modules) disclose at least two different mutually compatible binder prepaints useful for formulating a latex paint.
(a) the opacifying prepaint of claim 19 or 21; and	See claim 19 and 21. Both Brock (special effects module and dye module) and Heuwinkel (colour module and effect module) disclose at least two binder prepaints that also qualify as opacifying prepaints.

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(b) a latex polymeric binder prepaint	See claims 1(iii), 19 and 21. Brock (col. 4, line 14 to col. 7, line 33 (the binder module has latex polymeric binders (conventional film-forming resins such as (meth)acrylic copolymers, urethane polymers, polyesters, polyurethanes, binders based on cellulose)). Heuwinkel (page 6, line 27 to page 15, line 10 (the binder module has latex polymeric binders (conventional film-forming resins such as (meth)acrylic copolymers, urethane polymers, polyesters, polyurethanes, binders based on cellulose)).
having volume solids content of about 25% to about 70% or a Brookfield viscosity of less than about 100,000 centipoise at a shear rate of 1.25 reciprocal seconds, which prepaint consists essentially of a water-borne latex polymeric binder having a Tg of about -430° C. to about 70° C. and water;	See claims 19 and 21. Brock (col. 7, lines 22-23 (20%-60%)). Heuwinkel (page 6, line 13 (5%-99%) and page 7, lines 21-22 and 36-37 (Tg's of -50° C. to 150° C. and -20° C. to 75° C. respectively)). The Brookfield viscosity and the Tg are inherently within the disclosed ranges or would have been obvious from the disclosures because they are common to conventional paint.
wherein the prepaint ingredients are mutually compatible with each other and with the ingredients of the other prepaint in the set.	McClain (col. 3, lines 49-51 – no settling), Brock (col. 2, lines 36-40 – storage-stable), and Heuwinkel (page 5, lines 1-4 – storage-stable) each disclose binder prepaints having compatible ingredients that are also compatible with the ingredients of the paint.
33. The set of prepaints of claim 32, wherein the binder prepaint has a volume solids content of about 30 to about 65% and a Brookfield viscosity of about 100 to about 50,000 centipoise at a shear rate of 1.25 reciprocal seconds, and consists essentially of a water-borne polymeric binder having a Tg of about -10 to about 60° C.	Brock (col. 7, lines 22-23 (20%-60%)). Heuwinkel (page 6, line 13 (5%-99%) and page 7, lines 21-22 and 36-37 (Tg's of -50° C. to 150° C. and -20° C. to 75° C. respectively)). The Brookfield viscosity and the Tg are inherently within the disclosed ranges or would have been obvious from the disclosures because they are common to conventional paint.

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34. The set of prepaints of claim 32, wherein the binder prepaint further consists essentially of at least one additive selected from the group consisting of an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide, and antifreeze agent, the additive being present in an amount of less than about 10% by weight, based on the total weight of the prepaint.	<p>McClain (col. 3, lines 30-40; diatomaceous earth, limestone, calcined clay, dispersant, thickener, and coalescent), Brock (abstract and col. 7, lines 18-29; conventional additives, conventional solvents, water-miscible solvents, bases), and Heuwinkel (abstract and page 14, line 31 to page 15, line 10; conventional additives, conventional solvents, acids) each disclose a binder prepaint that further includes an additive from the group listed in claim 34.</p> <p>The Coatings Dictionary, pp. 348-49, Exhibit B, lists conventional paint additives from the group listed in claim 34. It would have been obvious from the disclosures of McClain, Brock and Heuwinkel to add conventional paint additives to the prepaints to modify the characteristics of the paint produced from the prepaints.</p>
35. A set of three different, but mutually compatible, fluid prepaints, useful for formulating a latex paint, which set comprises:	See claim 1.
(a) the set of prepaints of claim 32	See claim 32.
wherein the extender prepaint has a volume solids content of about 30% to about 70%, a PVC of about 35% to about 100%, and a Stormer viscosity of about 50 to about 250 KU; and	Claim 32 does not recite any extender prepaint so it is unclear what "the extender prepaint" refers to. Particularly because the next element (b) is an extender prepaint. Nevertheless, see claim 31(i) if "extender prepaint" is correct. If it was intended that "extender prepaint" was to be "opacifying prepaint", see claims 19 and 21.
(b) a fluid pigment extender prepaint which consists essentially of:	See claim 31.
(i) at least one mineral extender,	See claim 31(i).
(ii) at least one thickener,	See claim 31(ii).
(iii) water, and	See claim 31(iii).
(iv) optionally a polymeric binder.	See claim 31(iv).

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36. The set of prepaints of claim 35, wherein the extender prepaint has a volume solids content of about 35% to about 65%, a PVC of about 40% to about 100% and a Stormer viscosity of about 60 to about 150 KU:	See claim 31(i). Brock (col. 8, lines 9-10: volume solids content of dye module: 20%-80%; and col. 4, lines 9-10: volume solids content of special effect module: 10%-40%). Heuwinkel (page 6, lines 14-17: volume solids content of colour module: 0%-60%; volume solids content of effect module: 0%-50%; and volume solids content of rheology module: 0%-50%).
37. The set of prepaints of claim 32, wherein the extender prepaint further consists essentially of at least one additive selected from the group consisting of an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide and an antifreeze agent with the additive being present in an amount of less than about 20% by weight, based on the total weight of the prepaint.	Brock (col. 2, lines 5-10 and col. 2, line 49 to col. 4, line 13 and col. 7, line 36 to col. 8, line 13: special effect module and dye module each contain conventional additives, such as water-miscible solvents, defoamers, and neutralizing agents (which are acids and bases)), and Heuwinkel (abstract and page 15, line 12 to page 20, line 9: colour module and effect module each contain conventional additives such as water-miscible solvents, defoamers, and neutralizing agents (which are acids and bases)) each disclose at least two extender prepaints that further include an additive from the group listed in claim 37.  The Coatings Dictionary, pp. 348-49, Exhibit B, lists conventional paint additives from the group listed in claim 37. It would have been obvious from the disclosures of McClain, Brock and Heuwinkel to add conventional paint additives to the prepaints to modify the characteristics of the paint produced from the prepaints.
38. A paint line produced by a process which comprises the steps of:	See claim 5.
(a.) providing a set of different, but mutually compatible, fluid prepaints, which set comprises:	See claim 5(a).
(i.) at least one opacifying prepaint comprising at least one opacifying pigment,	See claim 5(i).
(ii.) at least one extender prepaint comprising at least one extender pigment, and	See claim 5(ii).

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(iii.) at least one binder prepaint comprising at least one latex polymeric binder; and	See claim 5(iii).
(b.) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.	See claim 5(b).
39. A set of different, but mutually compatible, fluid prepaints, sufficient to form at least one paint line useful as an elastomeric coating, which set comprises:	See claim 1. The '537 patent explains elastomeric coatings at col. 13, line 38 to col. 14, line 35. This information about elastomeric coatings and the formation of elastomeric coatings is knowledge common to the relevant art. Examples 36-41 of the '537 patent show examples of elastomeric coatings with the same basic ingredients used in the prepaints of each of McClain, Brock and Heuwinkel. It would have been obvious to form elastomeric coatings from a process similar to other surface coatings.
(i) at least one opacifying prepaint comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment; and	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of less than about 0° C.	See claim 1(iii). Heuwinkel expressly discloses use of a binder prepaint having a latex polymeric binder with a Tg of less than 0° C (Heuwinkel, page 7, lines 21-22 and 36-37 (Tg's of -50° C. to 150° C. and -20° C. to 75° C. respectively).
40. A method of forming at least one paint line useful as an elastomeric coating, which method comprises the steps of:	See claims 1 and 39.
(a) providing a set of different, but mutually compatible, fluid prepaints, which set comprises:	See claims 1 and 39.

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(i) at least one opacifying prepaint comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment; and	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymer binder having a Tg of less than about 0° C.; and	See claim 39(iii).
(b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.	See claim 5(b).
41. A method of forming a range of paints, the range comprising at least two paint lines useful as an elastomeric coating, which method comprises the steps of:	See claims 1, 6 and 39.
(a) providing a set of prepaints sufficient to formulate at least two paint lines, which set comprises:	See claim 6(a).
(i) at least one opacifying prepaint comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment;	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of less than about 0° C.; and	See claim 39(iii).

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(iv) at least one additional different prepaint selected from the group consisting of (i), (ii), (iii), and (iv); and	See claim 6(a)(iv).
(b) dispensing a predetermined amount each of the prepaints into containers or applicators to form the range of paints.	See claim 6(b).
42. A set of different, but mutually compatible, fluid prepaints sufficient to form at least one paint line useful as a non-cementitious, aggregate finish, which set comprises:	See claim 1. Aggregate is a well known additive for paint. It would have been obvious from the disclosures of any of McClain, Brock or Heuwinkel in light of Kitano to include aggregate as an additive to the paint or a prepaint. See also, Tsuei (col. 9, lines 43-65, col. 10, lines 24-48, and col. 16, lines 39-64).
(i) at least one opacifying prepaint comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment;	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymeric binder; and	See claim 1(iii).
(iv) at least one prepaint comprising an aggregate.	The '537 patent lists suitable aggregates at col. 12, lines 53-60. Aggregate is a well known additive for paint. Brock (col. 7, lines 42-47: dye module includes talc), Heuwinkel (abstract and page 15, line 31: colour module includes talcum) and Kitano (col. 2, lines 44-51: includes calcium carbonate, talc, glass powder, and silica sand; and col. 3, lines 27-35: includes glass beads) each disclose prepaints comprising an aggregate. It would have been obvious from the disclosures of any of McClain, Brock or Heuwinkel in light of Kitano to include aggregate as an additive to the paint or any prepaint. See also, Tsuei (col. 9, lines 43-65, col. 10, lines 24-48, and col. 16, lines 39-64).

U.S. Patent No. 6,531,537	Prior Art References
43. A method of forming at least one paint line useful as a non-cementitious, aggregate finish, which method comprises the steps of:	See claims 1, 5 and 42.
(a) providing a set of different, but mutually compatible, fluid non-cementitious prepaints, which set comprises:	See claim 42.
(i) at least one opacifying prepaint comprising at least one opacifying pigment;	See claim 1(i).
(ii) at least one extender prepaint comprising at least one extender pigment;	See claim 1(ii).
(iii) at least one binder prepaint comprising at least one latex polymeric binder; and	See claim 1(iii).
(iv) at least one prepaint comprising an aggregate; and	See claim 42(iv).
(b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.	See claim 5(b).
44. A method of forming a range of paints, the range comprising at least two paint lines useful as a non-cementitious, aggregate finishing coating, which method comprises the steps of:	See claims 1, 6 and 42.

U.S. Patent No. 6,531,537	Prior Art References
(a) providing a set of different fluid, but mutually compatible, non-cementitious prepaints sufficient to formulate at least two paint lines, which set comprises	See claims 6(a) and 42.
(i) at least one opacifying prepaint comprising at least one opacifying pigment;	See claim 1(i)
(ii) at least one extender prepaint comprising at least one extender pigment,	See claim 1(ii)
(iii) at least one binder prepaint comprising at least one latex polymeric binder,	See claim 1(iii)
(iv) at least one prepaint comprising an aggregate, and	See claim 42(iv).
(v) at least one additional different, prepaint selected from the group consisting of (i), (ii), (iii), and (iv); and	See claim 6(iv).
(b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the range of paints.	See claim 6(b).
45. A set of different, but mutually compatible, fluid prepaints sufficient to formulate at least one paint line	See claim 1.

U.S. Patent No. 6,531,537	Prior Art References
useful for forming pigmented and clear coatings, which set comprises:	McClain (col. 1, lines 11-22 and col. 2, lines 18-24) discloses a "neutral color" which includes a clear coating. Brock and Heuwinkel also disclose clear lacquers. It is unclear, however, how the "clear coating" of claim 45 is formed using an opacifying pigment prepaint of element 45(i). Opacifying pigments appear to not apply to clear coatings.
(i) at least one prepaint comprising at least one opacifying pigment; and	See claim 1(i).
(ii) at least two prepaints each of which comprises at least one latex polymeric binder.	See claim 1(iii). Each of McClain, Brock and Heuwinkel discloses at least two prepaints that each comprises at least one latex polymeric binder.
46. A set of different, but mutually compatible, fluid prepaints sufficient to form at least one paint line useful in graphics art applications, which set comprises:	See claim 1. The paints formed from any of McClain, Brock and Heuwinkel could also be used in graphics art applications.
(i) at least one prepaint comprising at least one latex polymeric binder having a Tg of about -50° C. to about 10° C.;	See claim 1(iii) and claim 39(iii). The specifically claimed Tg range is within the disclosed ranges or would have been obvious from the disclosures because they comprise latex polymeric binders common to conventional paint.
(ii) at least one prepaint comprising at least one latex polymeric binder having a Tg of about 50 to about 140° C.; and	See claims 1(iii) and 39(iii). Heuwinkel (page 7, lines 21-22 and 36-37) specifically discloses prepaints comprising latex polymeric binders ((meth)acrylic copolymers, polyurethane resins, and/or (meth)acrylated polyurethane resins) having Tg of -50° C. to 150° C and -20° C. to 75° C. Additionally, Landy uses a latex polymeric binder with a Tg above 0° C. The specifically claimed Tg range is within the disclosed ranges or would have been obvious from the disclosures because they comprise latex polymeric binders common to conventional paint.

U.S. Patent No. 6,531,537	Prior Art References
<p>(iii) optionally, at least one prepaint comprising at least one latex polymeric binder having a Tg of about 0° C. to about 65° C.</p>	<p>See claims 1(iii) and 39(iii).</p> <p>Heuwinkel at pp. 38-39 discloses four distinct binder modules each comprising different mixtures of latex polymeric binder components. Heuwinkel describes some examples of binder module prepaints used within the binder modules as having a Tg of -50° C. to 150° C (page 7, lines 21-22) and in other examples, a Tg of -20° C. to 75° C (page 7, lines 36-37 and page 28, line 4). For each of these examples, the resins used as binders are described as having specific characteristics within particular ranges that result in a Tg within the described range (for example, an average molecular weight, a hydroxyl value and an amine value). Each of the four specific binder module prepaint examples described in Heuwinkel has different characteristics which inherently result in different Tg values for each polymeric binder used. It is inherent within the disclosure of Heuwinkel, or at least obvious from the disclosure of Heuwinkel, to select latex polymeric binders having different Tg values for use in the binder prepaints of Heuwinkel so that resulting paints with different characteristics can be formed. It is known in the art to use different binders having different Tg values to produce paint with different characteristics.</p> <p>Additionally, Landy uses a latex polymeric binder with a Tg above 0° C. The specifically claimed Tg range is within the disclosed ranges or would have been obvious from the disclosures because they comprise latex polymeric binders common to conventional paint.</p>

U.S. Patent No. 6,531,537	Prior Art References
47. The set of prepaints of claim 46, which further comprises at least one additional prepaint selected from the group consisting of a prepaint comprising at least one alkali-soluble resin, a prepaint comprising at least one gloss additive, a prepaint comprising at least one wax, and at least one prepaint comprising at least one pigment dispersion.	See claim 6. It would have been obvious from the disclosures of McClain, Brock and Heuwinkel to have used an additional prepaint to achieve different finish characteristics or paint lines. Specifically, in addition to the four distinct binder module examples disclosed in Heuwinkel, Heuwinkel (page 6, line 27 to page 27, line 4) discloses a colour module, an effect module, a cross-linking module, and a rheology module that all include alkali-soluble resins (water-dilutable resins or anionic resins neutralized with bases that fall under the definition of an alkali-soluble resin in the '537 written description). Additionally, Brock (col. 2, line 49 to col. 4, line 13, col. 4, line 14 to col. 7, line 33, col. 7, line 34 to col. 8, line 13, col. 8, lines 14-26, and col. 8, line 27 to col. 9, line 17) discloses a special effect module, a dye module, a rheology module, and a cross-linking module that all include alkali-soluble resins (water-dilutable resins or anionic resins neutralized with bases that fall under the definition of an alkali-soluble resin in the '537 written description).
48. A method of forming at least one paint line, which method comprises the steps of:	See claim 5.
(a) providing the set of prepaints of claim 45, 46 or 47; and	See claims 45, 46, and 47.
(b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.	See claim 5(b).
49. The set of prepaints of claim 1, wherein the extender prepaint has a PVC of about 35% to about 100%.	See claim 31(i).
50. The method of forming at least one paint line of claim 5 wherein the extender prepaint has a PVC of about 35% to about 100%.	See claim 31(i).

In addition to the specific references mentioned in the Claims Chart above, there are many other references that disclose information material to the '537 patent which, when read in light of the other references cited above, further make obvious the claims of the '537 patents. Particularly, these references include the articles "Form Postponement" (Exhibit O), "Component Mixing" (Exhibit P), "Delayed Product Differentiation" (Exhibit Q), "Batch Processes" (Exhibit R) and "Paint Production" (Exhibit S).

The application of each of the unapplied prior art references to the claims of the '537 patent raises substantial new questions as to the patentability of the '537 patent. These references applied above were not applied to the '537 patent claims during prosecution and these glaring questions of patentability have not yet been addressed.

## V. CONCLUSION

Each of McClain, Brock and Heuwinkel anticipate the broadest claims of the '537 patent, and these patents in light of other prior art references make obvious the remaining claims of the '537 patent. Although McClain, Brock and Heuwinkel are shown on the face of the '537 patent, they were not applied to the patent claims. Application of the references to the claims raises significant questions of patentability and requires reexamination of the '537 patent.

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US006531537B2

(12) **United States Patent**  
Friel et al.(10) **Patent No.:** US 6,531,537 B2  
(45) **Date of Patent:** Mar. 11, 2003(54) **PREPAINTS AND METHODS OF  
PREPARING PAINTS FROM THE  
PREPAINTS**

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(52) **U.S. Cl.:** 524/497; 524/430; 524/432; 524/247; 524/284; 524/417; 524/445; 524/493

(58) **Field of Search:** 524/497, 430, 524/432, 297, 284, 417, 445, 493

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**ABSTRACT**

Methods of providing a paint line containing a latex polymeric binder are described. A range of paints can be formulated using sets of prepaints, at least one of which contains a latex polymeric binder. The paints may be applied as architectural coatings, industrial coatings, graphic arts coating, elastomeric coatings, and non-cementitious, aggregate finish coatings suitable for application on a wall directly or as a topcoat in exterior insulation finishing systems.

50 Claims, No Drawings

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**PREPAINTS AND METHODS OF  
PREPARING PAINTS FROM THE  
PREPAINTS**

**CROSS REFERENCE TO RELATED  
APPLICATIONS**

This application claims priority to U.S. Provisional Applications Ser. No. 60/183,655 filed Feb. 18, 2000, No. 60/183,656 filed Feb. 18, 2000 and No. 60/247,639 filed Nov. 10, 2000.

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

This invention relates to sets of prepaints methods of 15 formulating paint lines using its sets of prepaints, useful paints, including as architectural coatings, industrial coatings, graphic art coatings, elastomeric coatings and non-cementitious, aggregate finish coatings, from sets of prepaint compositions.

**2. Description of Related Art**

For decades, professional painters/contractors and do-it-yourself consumers have been able to purchase paints that are tinted at the point-of-sale rather than at the manufacturing facility. This postponement of product differentiation permits the buyer to specify the desired color of the paint from a wide variety of choices rather than a limited number of colors once produced by the paint manufacturer.

While not practiced commercially, it is also theoretically known in the paint industry to postpone product differentiation of the paint components themselves as long as possible in the paint manufacturing process. See, for example, Carola Grundfelt-Forsius' paper in *Faerg Lack Scand* 43(2), pages 5-6 (1997) which describes the use of intermediaries or components, i. e., mixtures of several of the paint raw material ingredients, that are mixed together with the tinting pastes to yield different types of paints. Grundfelt-Forsius provides an example of such a system employing a polyurethane binder for a solution polymer system.

The methods of postponement of product differentiation offers the buyer the flexibility of selecting the desired final paints, whether it be the color of the paint or the type of paint while at the same time permitting the paint manufacturer or seller (retail or wholesale or distributor) to minimize inventories of raw materials, intermediates and final products as well as stock outages.

Despite these benefits, paint manufacturers have only been able to successfully employ the postponement in product differentiation to paint systems based on solution polymers. Paint manufacturers have not been successful in postponing product differentiation of paint components in latex polymer-based paint systems. Since the majority of paints used today are based on latex polymers, there is a need for a practical method for postponing product differentiation in a latex polymer-based paint system.

It is considerably more difficult to formulate a stable paint when using latex emulsion polymers rather than solution polymers because of latex instability. Emulsion polymers are very sensitive to the solvents and surface active agents commonly found in paint formulations, such as surfactants, dispersants, rheology modifiers, and co-solvents. Solution polymers are by definition soluble in the solvent they are supplied in, and there is no thermodynamic driving force causing the polymer molecules to agglomerate or become unstable. In contrast, latex polymers contain the polymeric

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material in particles that are insoluble in water. These particles require considerable surface modifications to render them stable when supplied in an aqueous medium. If the surface modification is inadequate, the latex particles attach to one another forming a coagulated mass which then separates out of the latex paint. Paint formulating with a latex system is very difficult because the surface active materials in the formulation disrupt the delicate balance of surface forces that stabilize the latex particles in a water medium.

The difference between latex polymer systems (also referred to herein as "emulsion") and solution polymer systems is further explained in Temple C. Patton's book entitled *Paint Flow and Pigment Dispersion* (New York: John Wiley and Sons, Inc., 1979, pages 192-193). Here the author describes the drying processes for the two systems. The main difference lies in the time required for each polymer to reach an irreversible state. Latex polymers reach this state much faster than solution polymers and thus make paints based on latex polymers more difficult to stabilize than paints based on solution polymers. In discussing "solvent-type coatings", (which contain solution polymers) the author writes "... the liquid vehicle flows rather than deforms around the pigment particles on drying. This flow assists the compaction process as the film shrinks because of loss of volatile solvent. Although the vehicle becomes more viscous as solvent evaporates, flow persists through most of the drying cycle." As the author points out, the solution polymer is able to flow though most of the drying cycle as the solvent evaporates. This is not true for polymer emulsion. The same author notes: "... there is a preliminary flow of the latex suspension. This takes place before the time when the latex particles are first forced to come into intimate contact because of initial water loss. However, after this relatively short but very important initial flow, pigment compaction to achieve a high critical pigment volume concentration (CPVC) is achieved mainly by plastic deformation and coalescence of the latex particles." Coalescence is the irreversible contact between latex particles. Such irreversible contact can occur in a liquid paint based on latex polymers, but not in a liquid paint based on solution polymers. Thus, paints based on latex polymers are more difficult to formulate.

There is a great need to develop a set of prepaints and a method of formulating paints based on latex polymers using sets of prepaints.

Paint formulating involves the process of selecting and admixing appropriate paint ingredients in the correct proportions to provide a paint with specific processing and handling properties, as well as a final dry paint film with the desired properties. The major ingredients of latex paint formulations are a binder, an opacifying pigment, optional pigment extenders, and water. Common optional additives include defoamers, coalescents, plasticizers, thickeners, non-thickening rheology modifiers, opacifying agents, driers, anti-skinning agents, surfactants, mildewcides, biocides and dispersants. After the latex paint is formulated and applied to a surface, the paint dries by evaporation of the water, with or without the application of heat, and the binder forms a film containing therein the pigment and the pigment extender particles, if any.

Formulating paints is complex—it is not simply a matter of mixing a few paint ingredients in different ratios. Rather, it involves the selection and mixing of different paint ingredients in different ratios depending on the type of paint desired. This requires paint manufacturers to store many different paint ingredients and change paint ingredients

during manufacture depending on the specific paint type being prepared.

Furthermore, it requires those in the supply chain, especially the paint retailers, to carry a large inventory of paints in the warehouse and on the store shelves in order to offer a range of paints, such as various sheen levels, tint bases, paints for exterior use, paints for interior use, and paints of varying quality. It would be desirable to make paints, either at a relatively large-scale industrial plant or at a relatively smaller-scale, point-of-sale or point-of-use location using a limited number of paint ingredients to prepare all of these different paint formulations, thus, minimizing the number and type of paint ingredients needed to make a range of paints.

#### SUMMARY OF THE INVENTION

A "paint line", as used herein, includes at least two different paints which offer dried film properties which differ materially from each other in at least one observable property such as sheen, outdoor durability or color depth. A paint line may include, for example, three paints the dried films of which have different sheen levels, two paints the dried films of which have suitable interior or exterior performance, or four paints the dried films of which offer different quality or performance levels such as may be evidenced, for example, by different levels of scrub resistance.

A paint line could, more particularly, include four different paints, the dried films of which have different sheen levels, typically marketed as gloss; semi-gloss; eggshell, satin, or low lustre; and flat. The sheen is determined by the volume and type of the binder(s), pigment(s), and extender(s), if any, in the paint.

In addition to the various sheen levels, paints are commonly formulated to be neutral or accent (no or very low level of opacifying pigment), untinted (white) or tinted to a wide variety of colors using different tint bases, including pastel or light tones, medium or mid-tones, and deep tones. This capability requires a paint line having as many as five paints. Also, paints are formulated for exterior or interior use. And, paints are formulated to provide certain levels of performance properties, such as may be marketed as good/standard, better and best/premium.

Paint manufacturers and retailers typically offer a range of paints which including at least two paint lines. By "the range including at least two paint lines" herein is meant that the discrete elected levels of the observable property defining a first paint line are combined with the discrete elected levels of the observable property defining a second paint line, etc. to define the paints in the range of paints.

To prepare a range of paints which includes four paint lines may require preparing paints encompassing four sheen levels, four tint bases, interior and exterior use, and three quality levels. For all combinations 96 different paint formulations ( $4 \times 4 \times 2 \times 3$ ) may be needed. Also encompassed, however, is a range of paints in which certain of the defined paints, certain proportion, including up to as high as 10-60%, of the total number of paints, are selected to be omitted, for example, for commercial reasons or because they are not stable as defined herein. Further contemplated is a range of paints in which the observable properties of the dried paint films substantially, but not exactly, fulfill the standard definitions for example, the sheen of a dried outdoor mid-tone gloss paint in the standard, better, and premium lines may differ by a few points without departing from the meaning of a range of paints of this invention.

As used herein, "paint" is term used in its broadest sense and includes any coating that may be applied to a surface for

decorative, protective or both purposes. Specifically included are those systems employed for architectural coatings, industrial coatings, elastomeric coatings and non-cementitious, aggregate finish coatings employed as the topcoat over walls and in an exterior insulation and finishing system (referred to hereinafter as "EIFS").

As used herein, prepaints are "mutually compatible" if the paints formed by admixing the prepaints do not evidence signs of colloidal instability such as flocculation. Preferably, the paints formed from the prepaints exhibit less than 5 g of residue such as gel and grit per liter of paint when the paint is passed through a 325 mesh screen. More preferably, the paints formed from the prepaints exhibit less than 1 g of residue per liter of paint when the paint is passed through a 325 mesh screen. If the additives included to enhance specific paint properties, and colorants are fully compatible, i.e., they can be blended at any ratio without inducing colloidal instability, then they can be blended in any combination falling within the formulation space needed to achieve the desired property profile in the final paint. It is sufficient, however, for the prepaints, optional additives included to enhance specific paint properties, and colorants to be compatible, i.e., they can be blended at desired ratios without inducing colloidal instability to achieve the desired property profile in the range of paints.

In order to minimize the number of paint ingredients needed to prepare a range of paints one needs to consider the extremes of key properties required by the range of paints and formulate prepaints which are capable of being blended in various combinations to provide the key properties required, at their extreme values and at intermediate points as well. Specific properties may be improved by adding paint additives which enhance the desired property.

The above goal is achieved by employing a set of different, but mutually compatible, fluid prepaints sufficient to formulate at least one paint line. The set comprises (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; and (iii) at least one binder prepaint comprising at least one latex polymeric binder; Preferably, the number of prepaints is 3-15.

Also provided is a method of forming at least one paint line comprises the steps of:

(a) providing a set of different, but mutually compatible, fluid prepaints sufficient to formulate at least one paint line, which set comprises: (i) at least one opacifying prepaint including at least one opacifying pigment; (ii) at least one extender prepaint including at least one extender pigment; and (iii) at least one binder prepaint including at least one latex polymeric binder; and  
(b) dispensing a predetermined amount each of the prepaints into containers or applicator(s) to form the paint line.

Preferably, the total number of prepaints is 3-15.

The method may further include the step of mixing the prepaints before, while, or after they are dispensed into the containers or before or while they are dispensed into the applicator(s).

Further provided is a method of forming a range of paints. The range includes at least two paint lines. The methods comprises the steps of:

(a) providing a set of different, but mutually compatible, fluid prepaints sufficient to formulate the range of paints, which set comprises (i) at least one opacifying prepaint including at least one opacifying pigment; (ii) at least one extender prepaint including at least one extender pigment; (iii) at least one binder prepaint including at least one latex polymeric binder; and (iv) at least one additional

different prepaint selected from the group consisting of prepaints (i), (ii), and (iii); and

(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the paint lines.

Preferably, the total number of prepaints is 4-15.

The methods may further comprise the step of mixing the prepaints before, while, or after they are dispensed into the container or before or while they are dispensed into the applicator(s). The methods may further include the step of adjusting the viscosity of the dispensed prepaints before, while, or after they are dispensed into the container or before or while they are dispensed into the applicator(s) using a thickener, water, or a mixture thereof. The methods may further comprise the step of adding additional materials that enhance the application or final performance properties of the paint, including aggregates and thickeners. The methods may further include the step of adding at least one colorant to the dispensed prepaints. The methods may be carried out at a paint manufacturing facility, a point-of-sale, or a point-of-use and may be controlled by a computer.

In another embodiment, a set of different, but mutually compatible fluid prepaints sufficient to form at least one paint line useful as an elastomeric coating is provided. The set comprises (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; and (iii) at least one binder prepaint comprising at least one latex polymer binder having a Tg less than about 0° C.

Further provided is a method of forming at least one paint line useful as an elastomeric coating. The method comprises the steps of:

(a) providing a set of different, but mutually compatible, fluid prepaints, which set comprises (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; and (iii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg less than about 0° C.; and

(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the paint lines.

Further provided is a method of forming a range of paints. The range comprises at least two paint lines useful as elastomeric coatings. The method comprises the steps of:

(a) providing a set of different, but mutually compatible, fluid prepaints sufficient to formulate at least two paint lines, which set comprises: (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; (iii) at least one binder prepaint comprising at least one latex polymer binder having a Tg less than about 0° C.; and (iv) at least one additional different fluid prepaint selected from the group consisting of prepaints (i), (ii), and (iii); and

(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) devices to form the paint lines. In another embodiment, a set of different, but mutually compatible, fluid non-cementitious prepaints sufficient to form at least one paint line useful as a non-cementitious, aggregate finish is provided. The set comprises (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; (iii) at least one binder prepaint comprising at least one latex polymeric binder; and (iv) at least one prepaint comprising an aggregate.

Also provided is a method of forming at least one paint line useful as a non-cementitious, aggregate finish. The method comprises the steps of:

(a) providing a set of different, but mutually compatible, fluid non-cementitious prepaints, which set comprises: (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; (iii) at least one binder prepaint comprising at least one latex polymeric binder, and (iv) at least one prepaint comprising an aggregate; and

(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the paint line.

Further provided is a method of forming a range of paints. The range comprises at least two paint lines useful as a non-cementitious, aggregate finishing coatings. The method comprises the steps of:

(a) providing a set of different, but mutually compatible, fluid non-cementitious prepaints sufficient to formulate at least two paint lines, which set comprises: (i) at least one opacifying prepaint comprising at least one opacifying pigment; (ii) at least one extender prepaint comprising at least one extender pigment; (iii) at least one binder prepaint comprising at least one latex polymeric binder; (iv) at least one prepaint comprising aggregate; and (v) at least one additional different fluid prepaint selected from the group consisting of prepaints (i), (ii), (iii), and (iv); and

(b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the paint lines.

In another embodiment, a set of different, but mutually compatible, fluid prepaints sufficient to form at least one paint line useful for forming pigmented and clear coatings is provided. The set comprises: (i) at least one opacifying prepaint comprising at least one opacifying pigment; and (ii) at least two binder prepaints, each of which comprises at least one latex polymeric binder;

In another embodiment, a set of prepaints sufficient to form at least one paint line useful in graphics art applications is provided. The set comprises: (i) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of about -50° C. to about 10° C.; (ii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of about 50 to about 140° C.; and (iii) optionally at least one binder prepaint comprising at least one latex polymeric binder having a Tg of about 0° C. to about 65° C. The graphic art prepaints may further comprise additional fluid mutually compatible prepaints selected from the group consisting of: (i) a prepaint comprising at least one alkali soluble resin; (ii) a prepaint comprising at least one gloss additive; (iii) a prepaint comprising at least one wax; and (iv) a plurality of prepaints comprising at least one pigment dispersion.

If one paint line is desired, i.e., if one key property is varied (for example, sheen level, tint base, use type, or quality type), then the complete paint line can be made from one each of the opacifying prepaint (i), the extender prepaint (ii), and the binder prepaint (iii).

If a range of paints including two paint lines is desired, i.e., if two key properties are varied (for example, two selected from sheen level, tint base, use type, and quality type) then the range of paints may be made from at least one each of the opacifying, extender, and binder prepaints (i), (ii) and (iii) and at least one additional different prepaint selected from the opacifying, extender, and binder prepaints (i), (ii), and (iii), depending on which key properties are to be varied.

If a range of paints including three paint lines is desired, i.e., if three key properties are varied (for example, three selected from sheen level, tint base, use type, and quality type) then the range of paints can be made from at least one each of the opacifying, extender, and binder prepaints (i), (ii) and (iii) and at least two additional prepaints different opacifying, extender, or binder prepaints, depending on which key properties are to be varied.

If a range of paints including four paint lines is desired, i.e., if four key properties are varied (for example, sheen level, tint base, use type, and quality type) then the complete range of paints can be made from at least one each of the opacifying, extender, and binder prepaints (i), (ii), and (iii) different and at least three additional different prepaints, opacifying, extender, and binder, depending on which key properties are to be varied.

This technique may be continued to vary as many additional key properties as desired.

By "additional opacifying, extender, and binder prepaints" is meant a prepaint different from the opacifying, extender, and binder prepaints (i), (ii), and (iii), respectively, but otherwise meeting the limitations associated with prepaints.

As discussed above, "paint line" includes two or more different paints whose dried films differ materially from each other in at least one observable property. The paints are different from each other and must meet at least one of the following criteria:

- (1) the pigment volume concentration (PVC) of the paints which are most different must differ by at least 2%; or
- (2) the volume solids (VS) of the paints which are most different must differ by at least 2%.

The pigment volume concentration (PVC) is a measure of how "binder-rich" a formulation is. It is calculated herein using the following formula:

$$PVC(\%) = \frac{\text{volume of pigment(s)} + \text{volume extender(s)}}{\text{volume of pigment(s)} + \text{volume extender(s)} + \text{volume binder(s)}} \times 100$$

The volume solids (VS) is the dry volume of pigment(s) plus the dry volume of extender(s) plus the dry volume of binder(s). It is calculated herein by the following formula:

$$VS(\%) = \frac{\text{dry volume of pigment(s)} + \text{dry volume of extender(s)} + \text{dry volume of binder(s)}}{\text{total volume of formulation}} \times 100$$

If additives are present, their volume is not included in determining the total dry volume. In each of the above embodiments the prepaints are selected so that they cover a wide formulation space so that the desired final paint properties lie within the blend space defined by the prepaints at the extremes. In many cases the prepaints themselves will not be practical paints. But, by pushing the prepaints to these extremes one can maximize the blend space available for the set. When the prepaints, additives and colorants are all fully compatible, they can be blended at desired ratios to achieve the desired paint line(s) and range of paints without inducing colloidal instability. It is possible to make a specific paint in the paint line without utilizing each of the prepaints available in the set of prepaints. For example, a deep tone paint does not require the use of an opacifying pigment prepaint.

This technique is similar to the design principles used in statistical experimental design and analysis of mixture component designs; however, instead of designing a mixture

space to explore the response surface within it, one is designing the boundaries of the mixture space to maximize the flexibility of the paint system. The key to success is to have mutual compatibility of the individual prepaint ingredients and prepaints across the mixture space.

Paint properties can be predicted in a number of ways. One approach is to develop response surface models of the blend space using standard Mixture Component experimental design statistical tools. These simple statistical models can then be used by a linear optimization program, by a massive grid search or by a graphical analysis tool. Another approach is to simply use empirical methods to determine which blends are needed for specific paint lines, then incorporate those simple empirical recipes in the paint making machine software.

An extension of the techniques is to have the paint machine automatically pretest certain key properties (e.g., viscosity, forced dry gloss or color) and make minor adjustments during the formulating of a paint from the prepaints.

Having feedback loops in the paint machine can provide more precise matching of color, gloss, and viscosity targets.

Compatible paint ingredients can be combined in the various prepaints and the paints formed from the prepaints provide the properties characteristic of the amount of ingredient used.

It is preferred that the all fluid prepaints employed in the methods herein have the same or similar viscosities to aid in mixing.

The water-resistance, including blister resistance, wet adhesion, and scrub resistance of the paints prepared from the prepaint sets is expected to be improved because of the use of lower amounts of stabilizing materials such as surfactants which may be used relative to conventional formulating techniques. Further a line of paints or a range of paints prepared using the prepaints may react more predictably to added colorants, making color matching easier and facilitating the use of software for color matching. In addition, viscosity fluctuation in the final paint formulation is expected to be reduced because of the prior equilibration of ingredients in the prepaints.

The prepaints are formulated to maximize the flexibility of paint manufacturing. Rather than purchasing individual paint ingredients, paint manufacturers and even buyers at point-of-sale and point-of-use (paint stores, paint departments, and contractors), can purchase the set of prepaints to prepare a desired range of paints. These sets of prepaints will contain at least one each of prepaints x, y and z and possibly additional prepaints depending upon the formulating flexibility desired. Optionally, the above prepaints are mixed with an additional prepaint which includes at least one colorant, such as a colored pigment or dye.

The prepaint sets and formulating methods herein are not limited to the preparation of only latex paints. They may also be used to prepare any water-borne coating or related building products which require mixing ingredients, including, but not limited to, graphic arts, sealants, caulk, mastics, adhesives, architectural coatings (homeowner-applied and contractor-applied wall coatings, elastomeric wall and roof coatings and aggregate finish layers) and industrial coatings (such as those classified as original equipment manufacturing, maintenance, wood, metal, general industrial finishes, and other factory-applied coatings as well as a minor portion of non-architectural type coatings applied by do-it-yourselfers).

In the industrial coatings area, the methods herein may be applied to a broad range of coatings for automotive, marine, aircraft, other land transportation, appliances, metal

furniture, machinery & equipment, coil, metal containers, magnetic wire, concrete roof tile, insulating varnish, electronic, pipe, packaging, overprint, release, flatboard, wood furniture, plastic substrates, magnetic media, general metal, industrial maintenance, automotive refinish, traffic paint, fire retardant, aerosol, chemical agent resistant coating, roof, tank, deck, concrete, masonry water repellent, nail polish, art and hobby uses. For example, the method herein may be applied to produce a range of metal coatings, including flat, gloss, direct-to-metal, primer, mid-coat and solvent resistant coatings, using an appropriate set of pre-paints.

#### DETAILED DESCRIPTION OF THE INVENTION

In one embodiment of the opacifying prepaint, the prepaint is a fluid titanium dioxide prepaint which includes (i) at least one opacifying pigment, (ii) at least one dispersant, (iii) at least one thickener, and water. The dispersant(s) and the thickener(s) are compatible with the pigment(s) and with other optional paint ingredients. The prepaint has a volume solids content of about 30% to about 70%, preferably about 35% to about 50% and a Stormer viscosity of about 50 to about 250 KU, preferably about 60 to about 150 KU.

In an alternate embodiment, the opacifying prepaint is a fluid titanium dioxide prepaint useful for formulating a one pack, pigmented latex paint containing other paint ingredients. The prepaint includes (i) at least one opacifying pigment, (ii) at least one dispersant, (iii) at least one thickener, (iv) at least one film-forming or nonfilm-forming polymeric binder, and (v) water. The dispersant(s), the thickener(s), and the polymer(s) are compatible with the pigment(s) and with other optional paint ingredients. The prepaint has a volume solids content of about 30% to about 70%, preferably about 35% to about 50%, a PVC of about 35% to about 100%, preferably about 50% to about 100%, and a Stormer viscosity of about 50 to about 250 KU, preferably about 60 to about 150 KU. Preferably, the prepaint is stable to sedimentation, by which is meant herein that the pigment does not settle out after 10 days at 25° C. Optionally, the polymeric binder is adsorbed onto the opacifying pigment.

In one embodiment of the extender prepaint, it is a fluid pigment extender prepaint which includes (i) at least one mineral extender, (ii) at least one thickener, (iii) an optional polymeric binder, and (iv) water. The pigment extender prepaint has a volume solids content of about 30% to about 70%, preferably about 35% to about 65%, a PVC of about 35% to about 100%, preferably about 40% to about 100%, and a Stormer viscosity of about 50 to about 250 KU, preferably about 60 to about 150 KU. The prepaint ingredients are compatible with each other and with the ingredients of the other prepaints desired to be used therewith.

In one embodiment of the binder prepaint, it is a fluid latex polymeric binder prepaint which includes a water-borne latex polymeric binder having a Tg of about -40° C. to about 70° C., preferably about -10° C. to about 60° C., and water. The binder prepaint has a volume solids content of about 25% to about 70%, preferably about 30% to about 65%, and a Brookfield viscosity of less than about 100,000 centipoise, preferably about 100 to about 50,000 centipoise, at a shear rate of 1.25 reciprocal seconds. The prepaint ingredients are compatible with each other and with the ingredients of the other prepaints desired to be used therewith.

In the embodiments of prepaints the opacifying, extender, and binder prepaints (i), (ii), and (iii), it is optional to include

minor amounts, i.e., less than about 20% by weight, based on the total weight of the prepaint, of conventional paint additives including an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide, an antifreeze agent, a flash rust inhibitor, and the like. These additives must be compatible with the other paint ingredients in the prepaints and the paints employed in the methods herein.

Suitable opacifying pigments include white pigments which impart white scattering power to the paint across all visible wavelengths without a high degree of absorption. Pigment extenders are inorganic solids or opaque polymers which do not impart the primary color or hiding power to the paint although they may have secondary influences on those properties. The tint bases used for deep tone paints typically contain no or only very low levels of opacifying pigments.

Suitable opacifying pigments include titanium dioxide ( $TiO_2$ ) or a combination of titanium dioxide and auxiliary hiding pigments such as voided latex polymer particles, zinc oxide, lead oxide, a synthetic polymer pigment and mixtures thereof. Rutile and anatase grades of titanium dioxide are suitable for use herein. Rutile titanium dioxide is preferred. The surface of these titanium dioxides may be treated with various organic surface treatments and/or inorganic surface treatments, e.g., treatment with the oxides of silica, alumina, and zirconia. Fumed titanium oxide is also useful herein.

Suitable voided latex particles have a diameter of about 100 nm to about 2,500 nm and a void fraction of about 10% to about 75%. Preferably, the voided latex particles useful in the method of the invention have a particle size of about 500 nm to about 1,100 nm. OK particles have at least one void, but may have multiple voids, non-spherical voids, interconnected voids, voids having channels connected to the outside of the particles, and other structures described as vesiculated and spongelike. Preferably, the (Tg) have a single void. The particles have a glass transition temperature, as measured by differential scanning calorimetry at a rate of 20° C./min, of at least about 20° C., preferably at least about 50° C. The higher the Tg, the harder is the particle, making it less likely it is to collapse. If the voided latex particles collapse, they are unable to contribute to hiding. Voided latex particles may be prepared by conventional polymerization processes known in the art, such as those disclosed in U.S. Pat. No. 3,784,391, U.S. Pat. No. 4,798,691, U.S. Pat. No. 4,908,271, U.S. Pat. No. 4,972,000, U.S. Pat. No. 5,041,464, U.S. Pat. No. 5,157,084, U.S. Pat. No. 5,216,044 and U.S. Pat. No. 6,020,435, as well as Japanese Patent Applications 60/223, 873, 61/62510, 61/66710, 61/86941, 62/127336, 62/156387, 01/185311, and 02/140272. Preferably, the voided latex particles are prepared according to U.S. Pat. No. 4,427,836, U.S. Pat. No. 4,469,825, U.S. Pat. No. 4,594,363, U.S. Pat. No. 4,880,842, U.S. Pat. No. 5,494,971 and U.S. Pat. No. 6020,435.

Extender pigments useful herein include exterior and interior extender pigments optimized for the intended end use. Exterior extender pigments are not soluble in water and have a low absorption number. They are optimized for exterior durability in the particular market where the paint will be sold, and they do not detract from the desired non-cracking, non-chalking, and non-dirt-retaining properties of the dried paint. They also provide volume at a low cost. Interior extender pigments are optimized for hiding, gloss, and low cost. Suitable extender pigments include barium sulfate (1-15 microns), Blanc Fixe (0.5-5 microns), calcium carbonate (0.05-35 microns), silica (0.001-14 microns), magnesium silicate (0.5-15 microns), aluminum silicate (0.2-5 microns), nepheline syenite, mica, bentonite, magnesium alumino-silicate, fumed alumina, colloidal

attapulgite, synthetic amorphous sodium alumino-silicate, sodium potassium alumino-silicate, and the like.

Latex polymeric binders are polymers or prepolymers which form the primary paint film. They bind the pigment and/or extenders, provide the required paint flow, and determine the gloss and hardness of the final paint film. The binders selected for the prepaints will depend upon the final use of the formulated paints. Binders suitable for exterior paints are generally suitable for interior paints, but binders suitable for interior paints may not be suitable for exterior paints.

Suitable latex polymeric binders include, but are not limited to, homopolymers, copolymers or terpolymers such as, for example, acrylic and/or methacrylic polymers or copolymers, polyvinyl acetate, styrene-acrylic copolymers, styrene-butadiene, vinyl acetate-acrylic copolymers, ethylene-vinyl acetate copolymers, vinyl acetate-vinyl versatate copolymers, vinyl acetate-vinyl maleate copolymers, vinyl acetate-vinyl chloride-acrylic terpolymers, ethylene-vinyl acetate-acrylic terpolymers, and urethane polymers. The polymers may contain up to 10% by weight of functional monomers, (for example, but not limited to, carboxylic acid, phosphate, sulfate, sulfonate and amide) groups, other monomers, and mixtures thereof. Latex polymeric binders optionally incorporated in prepaints x, y, x', y', or other prepaints may be the same as or different from the latex polymeric binder of prepaint z.

It is conceivable that for industrial coatings the prepaints will employ a wide range of thermoplastic and thermosetting polymeric binders, that may be one-pot, two-pot or energy-curable, in the prepaints and methods of the inventions, including but not limited to: asphalt, paraffin wax, coal tar, alkyds, vinyl acetate, vinyl acetate/acrylic, styrene-butadiene, saturated polyester, unsaturated polyester, polyurethane, acrylic lacquer, acrylic enamel, acrylic latex, acrylic thermosetting, acrylic electrodeposition and autodeposition, styrene acrylic, vinyl toluene acrylic, radiation-curable acrylic, melamine, urea, epoxy (diglycidyl ether of bisphenol A, bisphenol F, cycloaliphatic, monofunctional epoxies and the like), vinyl acetate copolymer N-methylolacrylamide, vinyl acetate-ethylene, vinyl acetate terpolymer, vinyl acetate-vinyl versatate, polyvinyl chloride, polyvinylidene chloride, ethylene-acrylic acid, ethylene-methacrylic acid, ionomer, ethylene-methyl acrylate, celluloses, nitrocellulose, cellulose acetate butyrate, shellac, phenolic, ethyl silicate, polyacetals, styrene-allyl alcohol, chlorinated rubber, polyvinyl alcohol, butyl rubber, styrene—ethylene butylene—styrene block copolymer rubber, urethane acrylate, polyamideimide, polyesterimide, silicones, silanes, shellac, polyamides, polytetrafluoroethylene, polydiallyldimethylammonium chloride, polyphenylene sulfide, aromatic polyester, polyimide, siliconimide, fluoropolymers, parylene, aramid, stelarate polymers, oleoresinous, and chlorinated polyolefin and bis-cyclobenzobutene. The polymeric binders are preferably water-borne latexes, but may also be solvent-borne, water reducible, redispersible latexes, and combinations thereof.

The polymeric binders may be one-pack or two-pack. If the polymeric binders are two-pack, the polymeric binders may be used by:

- (1) separating one component of the two-pack system as a separate prepaint;
- (2) separating one component of the two-pack system and including it in either the opacifying prepaint or the extender prepaint;

- (3) adding one component of the two-pack system separately from any of the prepaints; and
- (4) combinations thereof.

Thickener is a general term used to describe any material added to a paint to modify its rheological profile. Preferred thickeners are associative thickeners. Suitable thickeners for use herein include polyvinyl alcohol (PVA), hydrophobically-modified, alkali soluble emulsions known in the art as HASE emulsions, alkali-soluble or alkali, swellable emulsions known in the art as ASE emulsions, hydrophobically, modified ethylene oxide-urethane polymers known in the art as HEUR thickeners, and cellulosic thickeners such as hydroxymethyl cellulose (HMC), hydroxyethyl cellulose (HEC), hydrophobically-modified hydroxy ethyl cellulose (HMHEC), sodium carboxymethyl cellulose (SCMC), sodium carboxymethyl 2-hydroxyethyl cellulose, 2-hydroxypropyl methyl cellulose, 2-hydroxyethyl methyl cellulose, 2-hydroxybutyl methyl cellulose, 2-hydroxyethyl ethyl cellulose, 2-hydroxypropyl cellulose, and the like. Also useful as thickeners are fumed silica, attapulgite clay and other types of clay, titanate chelating agents, and the like.

Suitable dispersants for use herein include non-ionic, anionic and cationic dispersants such as 2-amino 2-methyl 1-propanol (AMP), dimethyl amino ethanol (DMAE), potassium tripolyphosphate (KTPP), trisodium polyphosphate (TSPP), citric acid and other carboxylic acids, and the like. Also suitable for use as dispersants are Anionic polymers such as homopolymers and copolymers based on polycarboxylic acids, including those that have been hydrophobically- or hydrophilically-modified, e.g., polyacrylic acid or polymethacrylic acid or maleic anhydride with various monomers such as styrene, acrylate or methacrylate esters, diisobutylene, and other hydrophilic or hydrophobic comonomers as well as the salts of the aforementioned dispersants, and mixtures thereof.

Suitable defoamers include silicone-based and mineral oil-based defoamers, and the like.

Coalescents are not necessary if solvent-free latex polymer binders are used in the binder prepaints. Solvent-free binders typically have a low Tg and low minimum film-forming temperature so that they are film-forming at ambient temperatures, such as 20° C. If a coalescent is required, preferably it is incorporated in the binder prepaint and any other prepaints containing latex polymer binders.

Suitable coalescents, plasticizers, and other optional solvents include ethylene glycol, propylene glycol, hexylene glycol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TEXANOL™), glycol ethers, mineral spirits, methyl carbitol, butyl carbitol, phthalates, adipates, and the like.

Suitable mildewcides and biocides include zinc oxide, isothiazolones, triazoles, and the like.

Suitable surfactants include cationic, anionic, and non-ionic surfactants.

Suitable aggregates include small (typically 40 mesh and higher), intermediate (typically 20-40 mesh) and large (typically 20 mesh and lower) aggregates, such as sand, large particle size carbonates (limestone), ceramics, glass, fibers, coal, granite, talc, multicolored quartz, crushed sea shells, recycled products such as asphalt-containing materials, fiberglass, vermiculite, perlite, XO aggregate and the like.

Suitable flash rust inhibitors include aminoethylethanol amine, ammonium benzoate, sodium nitrite, ammonia benzoate, ammonium and amine salts of dicarboxylic acids and diphenols, such as glutaric acid, malonic acid, suberic acid, sebatic acid, adipic acid, succinic acid, phthalic acid, isophthalic acid, terephthalic acid, thidiphenol and sulfonyl-diphenol and their ammonium and amine-complexed zinc

salts, C-12 to C-14-tert-alkylamines, compounds with (2-benzothiazolylthio)-butanedioic acid; (2-benzothiazolylthio) butanedioic acid, 4-oxo-4-p-tolylbutyric acid adduct with 4-ethylmorpholine, zirconium complex with 4-methyl- $\delta$ -oxo-benzene-butanoic acid and the like.

Suitable crosslinkers include multivalent metal ions, such as zinc, magnesium, zirconium, calcium and like ions.

Reactive pigments are materials that are added to coating formulations to confer corrosion resistance by sacrificially corroding on behalf of the substrate. Suitable reactive pigments include calcium zinc phosphomolydate, zinc phosphate, aluminum triphosphate, strontium zinc phosphosilicate, molybdate-modified zinc phosphate and the like.

Suitable waxes include carnauba, paraffin, polyethylene, micronized ethylene-acrylic acid, polytetrafluoroethylene (PTFE), and the like.

Alkali-soluble resins are polymers that contain sufficient acid functionality and low enough molecular weights to dissolve in an aqueous media when neutralized with base. They exhibit Newtonian rheology, and act as a dispersant (i.e., reduce the surface tension of the aqueous medium). Suitable alkali-soluble resins include esters of acrylic acid and methacrylic acid copolymerized with carboxylic acid monomers (such copolymers, for example, are available from the Rohm and Haas Company and sold under the trade names Acrysol™ I-62 and Acrysol™ I-2074), copolymers of styrene and acrylic acid with optional alpha-methyl styrene (such polymers, for example, are available from the Rohm and Haas Company and sold under the trade name Morez™ 101), styrene/maleic anhydride copolymers, and the like.

In another preferred embodiment, the prepaints and methods of the present invention may be used to make elastomeric coatings suitable for either wall or roof applications. These prepaints may be mixed in various ratios to obtain elastomeric coatings of different quality, flexibility, mildew protection, and substrate adhesion suitable for either application on wall or roofs.

The main feature that distinguishes elastomeric coatings from typical architectural coatings is the use of binders with low temperature ( $<0^\circ$  C.) flexibility and the thickness at which the coating is applied (typically a dry coating thickness of about 6 to about 20 mil for wall applications and about 15 to about 40 mil for roof applications). Low temperature flexibility is particularly desirable for elastomeric coatings when they are being used over walls that may develop cracks, such as masonry walls, or roofing substrates that have a high degree of dimensional variance with climate. In addition to coating flexibility, it is desirable to have an elastomeric coating line with different degrees of low temperature flexibility, different qualities, ability to adhere to different substrates, and variations in appearance.

For a climate that experiences freezing temperatures through the winter, the following characteristics can be used to describe the different quality levels:

#### Quality Level

Description	PVC	TiO <sub>2</sub> PVC	Flexibility Temperature
high	<40	>5	<0° F.
medium	<40	4-5	<0° F.
medium	>40	>5	<0° F.
low	>40	<4	<0° F.

For a climate that has only a few days of freezing temperatures through the winter, the following characteristics can be used to describe the different quality levels:

#### Quality Level

5	Description	PVC	TiO <sub>2</sub> PVC	Flexibility Temperature
high	<40	>5	<0° F.	
medium	<40	4-5	<32° F.	
medium	>40	>5	<37° F.	
low	>40	<4	<32° F.	
10	poor	>40	>4	<40° F.

The quality of the elastomeric coating may be varied further depending on whether or not zinc oxide (ZnO) is present in the formulation. Zinc oxide changes the mechanical properties of the coating.

Finally, the elastomeric coating may be further varied through the addition of colorants. Typically, these colorants are dry ground and made in the coating grind portion.

For elastomeric coatings, one may define the following properties that may be varied in the coating manufacture to make different elastomeric coatings: coating flexibility, coating quality (durability), substrate adhesion and appearance

To differentiate based on the flexibility of the elastomeric coating, one may adjust the Tg of the binder, the PVC of the coating, and the presence and level of zinc oxide. To differentiate based on the durability of the elastomeric coating, one may adjust the level of titanium dioxide (TiO<sub>2</sub>). To differentiate based on the adhesion of the elastomeric coating to a substrate, one may formulate to coat a wall or a roof by varying the binder composition and level. To differentiate based on the appearance of the elastomeric coating, one may adjust the level and type of colorant. To obtain these different properties one may prepare a set of prepaints as set forth in Examples 36-41 below, and mix them in appropriate quantities to make elastomeric coatings that vary the properties described above.

In another preferred embodiment, the prepaints and methods herein may be used to make non-cementitious, aggregate finish coatings suitable for application on a wall directly or as a topcoat in exterior insulation and finishing systems (EIFS). These prepaints or preformulated components may be mixed in various ratios to obtain coatings of different flexibility, quality (durability), color, and texture.

The following formulation properties provide an example of how one may influence the durability of its non-cementitious, aggregate finish coatings used specifically for EIFS. Other types of aggregate finishes may have different ranges of PVC that correspond to different qualities. Therefore, the description below is only meant to be an example for aggregate finish coatings used in EIFS, and is not meant to define the PVC levels used in other non-cementitious, aggregate finish coatings.

#### Quality

55	Description	PVC
high	<72	
medium	72-77	
low	>77	

In addition, one may define the following formulation properties that affect color strength. Other types of aggregate finishes may have different TiO<sub>2</sub> levels that correspond to different color strengths. Therefore, the description below is only meant to be an example for aggregate finish coatings used in EIFS, and is not meant to define TiO<sub>2</sub> levels used in other aggregate finishes.

Description	TiO <sub>2</sub> PVC(%)
white, pastels	>1.5
midtones	0.5-1.5
deep tones	<0.5

Finally, one may also define the following formulation properties that affect coating texture.

Description	Small Aggregate	Large Aggregate
fine	>90%	≤10%
coarse	≤90%	>10%

Further variations in aggregate finish performance can be achieved by varying binder flexibility or T<sub>g</sub>.

As a specific embodiment of this invention relating to non-cementitious, aggregate finish coatings, one may vary the following properties in the coating manufacture to make different coatings: PVC level, TiO<sub>2</sub> level, Aggregate ratio and Binder T<sub>g</sub>.

To differentiate based on the flexibility of the non-cementitious, aggregate finish coatings, one may adjust the T<sub>g</sub> of the binder. To differentiate based on the durability of the non-cementitious, aggregate finish coatings, one may adjust the PVC of the coating. To differentiate based on the color of the non-cementitious, aggregate finish coatings, one may adjust the level of TiO<sub>2</sub> and the type and level of colorant. To differentiate based on the texture of the non-cementitious, aggregate finish coatings, one may adjust the size and level of the large aggregate and the ratio of the large aggregate to small aggregate. To obtain these different properties one may prepare a set of prepaints as set forth in Examples 54-58 below, and mix them in appropriate quantities to make non-cementitious, aggregate finish coatings that vary the properties described above.

In another preferred embodiment, the prepaints may be used in the methods of the invention to form a range of coatings useful where some of the coatings contain opacifying and/or extender pigments and where some of the coatings do not contain opacifying pigments ("clears"). These coatings may be applied over a variety of substrates, including metal, wood, and cementitious substrates, such as concrete roof tiles.

In another preferred embodiment, the prepaints may be used in the methods herein to form a range of graphic arts paint lines useful for a number of applications including, but not limited to, inks for giftwrap paper, corrugated substrate, newsprint, paperboard, labels, freezer bags, storage bags, metal films, foils; as well as overprint coatings applied for general purposes such as water-resistance, rub-resistance and high slip.

All ranges disclosed herein are inclusive and the minimums and maximums of the nested ranges are combinable. Test Procedures

The Stormer viscosity of the prepaints is measured using ASTM method D562. The Brookfield viscosity of the binder prepaints and final paints is measured using spindle #4 of a Brookfield viscometer at 6 rpm. The ICI viscosity of the prepaints and paints is measured using ASTM method D3205-77. Glass transition temperature ("T<sub>g</sub>") may be measured via differential scanning calorimetry at a rate of 20° C./minute.

## Example 1

5 This example describes the preparation of a white pre-paint which was prepared by combining the following ingredients:

10	Ingredient	Amount (lbs./100 gallons)
Pigment - Titanium Dioxide Slurry (76.5% solids) (Ti-Pure™ R-746 - DuPont)	1152.25	
15 Dispersant (Tanol™ 1124 - Rohm and Haas)	7.06	
Defoamer (Drewplus™ L-475)	1.00	
Binder Acrylic (50% solids - Tg 28° C.) (Rhoplex™ SG-10M - Rohm and Haas)	166.32	
Opacifier - Voided Latex Particles (Ropaque™ OP-96 - Rohm and Haas)	151.80	
20 Coalescent (Texanol™)	12.95	
Rheology Modifier (Acrysol™ RM-8W - Rohm and Haas)	12.76	
Base - Ammonia (28%)	1.65	

25 The prepaint was prepared using a laboratory mixer having a 45° pitch stirring blade. The water, dispersant, and defoamer, were combined and mixed. The titanium dioxide slurry was slowly added and the mixture was stirred for 15-20 minutes. The binder, coalescent, rheology modifier, 30 ammonia, and additional water if necessary were then added.

The resulting prepaint had a total volume of 100 gallons, 35 total weight of 1,505.8 lbs., total PVC of 80.0%, volume solids of 44.0%, weight solids of 67.1%, density of 15.058 lbs./gallon, 0.40% dispersant on pigment solids, and 10.0% coalescent on latex solids. Its initial and equilibrated Stormer viscosities were 88 and 90 KU. Its initial and equilibrated pH values were 8.8 and 8.6.

## Example 2

40 This example describes the preparation of an exterior pigment extender prepaint. It was prepared as above by 45 combining the following ingredients:

50	Ingredient	Amount (lbs./100 gallons)
Pigment - Nepheline Syenite (7.5μ) (Minex™ 4)	784.30	
Dispersant (Tanol™ 1124 - Rohm and Haas)	7.84	
Defoamer (Drewplus™ L-475)	2.00	
Binder Acrylic (53.5% solids - Tg 18° C.) (Rhoplex™ ML-200 - Rohm and Haas)	157.49	
55 Coalescent (Texanol™)	5.90	
Rheology Modifier (Acrysol™ RM-8W - Rohm and Haas)	2.55	
Water	368.86	

60 The resulting prepaint had a total volume of 100 gallons, 65 total weight of 1,328.9 lbs., total PVC of 80.0%, volume solids of 45.0%, weight solids of 65.4%, density of 13.29 lbs./gallon, 0.50% total dispersant on pigment solids and 7.0% total coalescent on binder solids. The initial and equilibrated Stormer viscosities were 90 and 93. The initial and equilibrated pH values were 8.9 and 8.7.

## Example 3

This example describes the preparation of an interior pigment extender prepaint which was prepared as described above by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Pigment - Calcium Carbonate (12 $\mu$ ) (Omyacarb™ 12)	405.67
Pigment - Calcium Carbonate (3.2 $\mu$ ) (Vicron™ 15-15)	203.59
Pigment - Aluminum Silicate (1.4 $\mu$ ) (Optiwhite™)	165.41
Dispersant (Tanol™ 1124 - Rohm and Haas)	7.75
Defoamer (Drewplus™ L-475)	1.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES™ 3803 - Rohm and Haas)	157.61
Coalescent (Texanol™)	6.07
Rheology Modifier - HEUR (Acrysol™ RM-2020-NPR)	17.53
Base - Ammonia (28%)	0.87
Water	356.59

The resulting prepaint had a total volume of 100 gallons, total weight of 1,322.1 lbs., total PVC of 80%, volume solids of 45%, weight solids of 65.15%, density of 13.2210 lbs./gallon, 0.50% dispersant on pigment solids, and 7.00% coalescent on binder solids. Its initial and equilibrated Stormer viscosities were 91 and 89. Its initial and equilibrated pH values were both 9.2.

## Example 4

This example describes a vinyl acetate/acrylic latex polymer binder prepaint which was prepared as described above except that the binder, defoamer, coalescent, ammonia, water, and rheology modifier were combined and mixed. The ingredients and amounts were as follows:

Ingredient	Amount (lbs./100 gallons)
Defoamer (Drewplus™ L-475)	8.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES™ 3803 - Rohm and Haas)	788.06
Coalescent (Texanol™)	30.34
Rheology Modifier - HEUR (Acrysol™ SCT-275 - Rohm and Haas)	3.02
Base - Ammonia (28%)	1.95
Water	60.08

The resulting prepaint had a total volume of 100 gallons, total weight of 891.5 lbs., volume solids of 45.0%, a weight solids of 48.6%, a density of 8.91 lbs./gallon and 7.0% coalescent on binder solids. Its initial and equilibrated Stormer viscosities were 88 and 90. Its initial and equilibrated pH values were 8.6 and 8.4. Its equilibrated Brookfield viscosity should be less than 10,000 cps.

## Example 5

This example describes a flat acrylic binder prepaint which was prepared as above by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Defoamer (Drewplus™ L-475)	8.00
Binder - Acrylic (53.5% solids - Tg 18° C.) (Rhoplex™ ML-200 - Rohm and Haas)	769.96
Coalescent (Texanol™)	28.83
Rheology Modifier (HEUR) (Acrysol™ RM-8W - Rohm and Haas)	1.15
Base - Ammonia (28%)	.57
Solvent - Propylene Glycol	60.00
Water	12.84

15 The resulting prepaint had a total volume of 100 gallons, total weight of 881.4 lbs., volume solids of 44.0%, weight solids of 46.7%, density of 8.81 lbs./gallon, and 7.0% coalescent on binder solids. Its initial and equilibrated Stormer viscosities were 91 and 89. Its initial and final pH 20 values were both 8.9/9.0. Its equilibrated Brookfield viscosity should be less than 10,000 cps.

## Example 6

25 This example describes a gloss acrylic binder prepaint which was prepared as described above by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Defoamer (Drewplus™ L-475)	8.00
Binder - Acrylic (50% solids - Tg 28° C.) (Rhoplex™ SG-10M - Rohm and Haas)	737.08
Coalescent (Texanol™)	36.85
Rheology Modifier - HEUR (Acrysol™ RM 8W - Rohm and Haas)	11.62
Base - Ammonia (28%)	.35
Solvent - Propylene Glycol	60.00
Water	21.26

40 The resulting prepaint had a total volume of 100 gallons, a total weight of 875.2 lbs., volume solids of 39.0%, a weight solids of 42.11%, a density of 8.75 lbs./gallon and 10.0% coalescent on binder solids. Its initial and equilibrated Stormer viscosities were 97 and 98. The initial and equilibrated pH values were 9.0. Its equilibrated Brookfield viscosity should be less than 10,000 cps.

## Example 7

45 This example describes the preparation of a white pigment prepaint including a solvent-free acrylic binder and without the use of a coalescent. The ingredients are mixed as described in Example 1 using the ingredients and amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Pigment - Titanium Dioxide (Ti-Pure™ R-706 - DuPont)	734.49
Opacifier - Voided Latex Particles (Ropaque™ OP-96 - Rohm and Haas)	164.43
Dispersant (Tanol™ 731 - Rohm and Haas)	29.38
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide (Kathon™ LX (1.5%) - Rohm and Haas)	2.00

-continued

Ingredient	Amount (lbs./100 gallons)
Defoamer (Foamaster™ VL)	3.00
Binder - Acrylic copolymer (43.5% solids - Tg -2° C.) (Rboplex™ SF-012 - Rohm and Haas)	165.96
Rheology Modifier - HEUR (Acrysol™ RM-825 - Rohm and Haas)	5.00
Rheology Modifier - HEUR (Acrysol™ RM-2020 NPR - Rohm and Haas)	42.69
Base - Ammonia (28%)	.49
Water	250.13

The resulting prepaint should have a total volume of 100 gallons, total weight of 1,401.3 lbs., total PVC of 80.0%, volume solids of 40.0%, weight solids of 61.1% density of 14.01 lbs./gallon, and 1.0% dispersant on pigment solids. Its estimated Stormer viscosity is 102 KU. Its pH should be 8.5-9.0.

## Example 8

This example describes the preparation of an exterior pigment extender prepaint with a solvent-free acrylic binder without the use of a coalescent. The ingredients are mixed as described in Example 1 using the ingredient amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Pigment - Nepheline Syenite (7.5 $\mu$ ) (Minex™ 4)	697.16
Dispersant (Tamoil™ 731 - Rohm and Haas)	27.89
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide (Kathon™ LX (1.5%) - Rohm and Haas)	2.00
Defoamer (Foamaster™ VL)	3.00
Binder - Acrylic (46.5% solids - Tg 1° C.) (Primal™ SF-015 Rohm and Haas)	160.84
Rheology Modifier HEUR (Acrysol™ RM-2020 NPR - Rohm and Haas)	101.80
Water	284.47

The resulting prepaint should have a total volume of 100 gallons, total weight of 1,280.9 lbs., total PVC of 80.0%, volume solids of 40.0%, weight solids of 60.27%, density of 12.81 lbs./gallon, and 1.0% dispersant on pigment solids. Its Stormer viscosity should be 95 KU. Its pH should be 8.5-9.0. If not, the pH is adjusted as described in Example 7.

## Example 9

This example describes the preparation of an interior pigment extender prepaint including a solvent-free vinyl acetate/acrylic binder without the use of a coalescent. The ingredients are mixed as described in Example 1 using the ingredient amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Pigment - Calcium Carbonate (3.2 $\mu$ ) (Snowflake™)	451.20
Pigment - Aluminum Silicate (1.4 $\mu$ ) (Optiwhite™)	220.37
Dispersant (Tamoil™ 1254 - Rohm and Haas)	19.19
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide (Kathon™ LX (1.5%))	2.00

-continued

Ingredient	Amount (lbs./100 gallons)
Defoamer (Foamaster™ VL)	3.00
Binder - Vinyl Acetate/Acrylic (55% solids) (Rovace™ 9900)	139.86
Rheology Modifier HASE (Acrysol™ DR-3)	9.00
Base - Ammonia (28%)	0.86
Water	405.69

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,254.9 lbs., total PVC of 80.0%, volume solids of 40.0%, weight solids of 59.65%, density of 12.55 lbs./gallon, and 1.0% dispersant on pigment solids. Its Stormer viscosity should be 95 KU. Its pH should be 8.5-9.0.

## Example 10

This example describes the preparation of a vinyl acetate/acrylic latex polymer binder prepaint including a solvent-free vinyl acetate/acrylic binder without a coalescent. The ingredients are mixed as described in Example 4 using the ingredient amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 10° C.) (Rovace™ 9900 - Rohm and Haas)	699.25
Defoamer (Foamaster™ VL)	3.00
Rheology Modifier HASE (Acrysol™ DR-3 - Rohm and Haas)	12.96
Base - Ammonia (28%)	2.90
Water	405.69

The resulting prepaint should have a total volume of 100 gallons, total weight of 885.2 lbs., volume solids of 40.0%, a weight solids of 43.5%, and density of 8.85 lbs./gallon. Its Stormer viscosity should be 99 KU. Its Brookfield viscosity should be less than 10,000 cps. Its pH should be 8.5-9.0.

## Example 11

This example describes the preparation of a flat latex polymer binder prepaint including a solvent-free acrylic binder and no coalescent. The ingredients are mixed as described in Example 4 using the ingredient amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Defoamer (Foamaster™ VL)	8.00
Binder - Acrylic Copolymer (43.5% solids - Tg -2° C.) (Rboplex™ SF-012 - Rohm and Haas)	723.77
Rheology Modifier - HEUR (Acrysol™ RM - 2020 NPR - Rohm and Haas)	3.00
Water	133.75

The resulting prepaint should have a total volume of 100 gallons, a total weight of 868.5 lbs., volume solids of 36.0%, weight solids of 38.8% and density of 8.69 lbs./gallon. Its Stormer viscosity should be 99 KU. Its Brookfield viscosity should be less than 10,000 cps. Its pH should be 8.5-9.0 and, if not, it is adjusted as discussed above.

## Example 12

This example describes the preparation of a gloss latex polymer binder prepaint using a solvent-free acrylic binder

and no coalescent. The ingredients are mixed as described in Example 4 using the ingredient amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Defoamer (Foamaster™ VL)	8.00
Binder - Acrylic Copolymer (43.5% solids - Tg -2° C.) (Rhoplex™ SF-012 - Rohm and Haas)	767.57
Rheology Modifier - HEUR (Acrysol™ RM-2020 NPR - Rohm and Haas)	23.00
Water	61.62

The resulting prepaint should have a total volume of 100.0 gallons, total weight of 860.4 lbs, volume solids of 37.0%, a weight solids of 38.8% and a density of 8.60 lbs/gallon. Its Stormer viscosity should be 99 KU. Its Brookfield viscosity should be less than 10,000 cps. Its pH should be 8.5-9.0 and, if not, it should be adjusted as described above.

#### Example 13

This example describes the preparation of a white pigment prepaint using an interior gloss grade titanium dioxide which was prepared by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Pigment - Titanium Dioxide (Ti-Pure™ R-900 - DuPont)	734.49
Opacifier - Voided Latex Particles (30.5% solids) (Ropaque™ Ultra-Rohm and Haas)	164.43
Dispersant (Tamol™ 1254 - Rohm and Haas)	20.99
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide (Kathon™ LX (1.5% - Rohm and Haas)	2.00
Defoamer (Foamaster™ VL - source)	3.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES 3083 - Rohm and Haas)	140.10
Coalescent (Texanol™)	11.37
Rheology Modifier - HASE (Acrysol™ DR-3)	11.47
Base - Ammonia (28%)	1.20
Solvent - Propylene Glycol	50.00
Water	264.38

The resulting prepaint had a total volume of 100 gallons, a total weight of 1405.4 lbs, total PVC of 80%, volume solids of 40%, weight solids of 61.25%, density of 14.05 lbs/gallon, 1.0% dispersant on pigment solids, and 9.0% coalescent on binder solids. The Stormer viscosity was 100 KU. The Brookfield viscosity was 15,300 cps. The pH was 8.8.

#### Example 14

This example describes the preparation of a white pigment prepaint using an exterior gloss grade titanium dioxide which was prepared by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Pigment - Titanium Dioxide (Ti-Pure™ R-706 - DuPont)	734.56
Opacifier - Voided Latex Particles (30.5% solids) (Ropaque™ Ultra-Rohm and Haas)	164.44
Dispersant (Tamol™ 731- Rohm and Haas)	29.38

-continued

Ingredient	Amount (lbs./100 gallons)
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide (Kathon™ LX (1.5% - Rohm and Haas)	2.00
Defoamer (Foamaster™ VL)	3.00
Binder - Acrylic Copolymer (50% solids - Tg 28° C.) (Rhoplex™ SG-10 - Rohm and Haas)	151.20
Coalescent (Texanol™)	12.49
Rheology Modifier) HEUR (Acrysol™ RM-2020 NPR - Rohm and Haas)	42.69
Base - Ammonia (28%)	.49
Solvent - Propylene Glycol	50.00
Water	211.34

The resulting prepaint had a total volume of 100 gallons, a total weight of 1403.6 lbs, total PVC of 80%, volume solids of 40%, weight solids of 61.2%, density of 14.04 lbs/gallon, 1.0% dispersant on pigment solids, and 9.0% coalescent on binder solids. The Stormer viscosity was 100 KU. The Brookfield viscosity was 4,010 cps. The pH was 8.8.

#### Example 15

This example describes the preparation of an exterior pigment extender prepaint. It was prepared by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Pigment - Nepheline Syenite (7.5 $\mu$ ) (Minex™ 4)	697.16
Dispersant (Tamol™ 731 - Rohm and Haas)	27.89
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide Kathon™ LX (1.5% - Rohm and Haas)	2.00
Defoamer (Foamaster™ VL)	3.00
Binder - Acrylic (53.5% solids - Tg 18° C.) (Rhoplex™ Multilobe 200 - Rohm and Haas)	139.98
Coalescent (Texanol™)	5.24
Rheology Modifier - HEUR (Acrysol™ RM - 2020 - Rohm and Haas)	101.80
Solvent - Propylene Glycol	50.00
Water	254.40

The resulting prepaint had a total volume of 100 gallons, a total weight of 1281.5 lbs, total PVC of 80.0%, volume solids of 40.0%, weight solids of 60.3%, density of 12.81 lbs/gallon, 1.0% dispersant on pigment solids, and 7.0% total coalescent on binder solids. The Stormer viscosity was 96 KU. The Brookfield viscosity was 7,210 cps. The pH was 9.8.

#### Example 16

This example describes the preparation of an interior pigment extender prepaint. It was prepared by combining the following ingredients:

Ingredients	Amounts (lbs./100 gallons)
Pigment - Calcium Carbonate (5 $\mu$ ) (Snowflake™)	451.20
Pigment - Aluminum Silicate (1.4 $\mu$ ) (Optiwhite™)	220.37

-continued

Ingredients	Amounts (lbs./100 gallons)
Dispersant (Tamol™ 1254 - Rohm and Haas)	19.19
Non-ionic Surfactant (Triton™ CF-10)	2.00
Biocide (Kalibor™ LX (1.5%)) - Rohm and Haas)	2.00
Defoamer (Foamaster™ VL)	3.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES 3083 - Rohm and Haas)	140.10
Coalescent (Texanol™)	6.93
Rheology Modifier - HASE (Acrysol™ DR-3 - Rohm and Haas)	11.00
Base - Ammonia (28%)	0.86
Solvent - Propylene Glycol	50.00
Water	348.48

The resulting prepaint had a total volume of 100 gallons, a total weight of 1255.1 lbs, total PVC of 80.0%, volume solids of 40.0%, a weight solids of 59.7%, density of 12.55 lbs/gallon, 1.0% dispersant on pigment solids, and 9.0% total coalescent on binder solids. The Stormer viscosity was 102 KU. The Brookfield viscosity was 3,410 cps. The pH was 8.9.

## Example 17

This describes the preparation of a vinyl acetate/acrylic binder prepaint. It was prepared by combining the following ingredients:

Ingredients	Amounts (lbs./100 gallons)
Defoamer (Foamaster™ VL)	3.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES 3083 - Rohm and Haas)	700.48
Coalescent (Texanol™)	34.67
Rheology Modifier - HASE (Acrysol™ DR-3 - Rohm and Haas)	12.96
Base - Ammonia (28%)	2.90
Solvent - Propylene Glycol	50.00
Water	83.48

The resulting prepaint had a total volume of 100 gallons, a total weight of 887.5 lbs, volume solids of 40.0%, a weight solids of 43.4%, a density of 8.88 lbs/gallon, 9.0% coalescent on binder solids. Its Stormer viscosity was 98.0. The Brookfield viscosity was 13,600 cps. Its pH was 9.0.

## Example 18

This example describes the preparation of a flat acrylic binder prepaint. It was prepared by combining the following ingredients:

Ingredients	Amounts (lbs./100 gallons)
Defoamer (Foamaster™ VL)	3.00
Binder - Acrylic (53.5% solids - Tg 18° C.) (Rhoplex™ Multilobe 200 - Rohm and Haas)	699.92
Coalescent (Texanol™)	26.21
Rheology Modifier - HEUR (Acrysol™ RM-2020-NPR - Rohm and Haas)	1.44

-continued

Ingredients	Amounts (lbs./100 gallons)
Base - Ammonia (28%)	0.35
Solvent - Propylene Glycol	50.00
Water	96.59

The resulting prepaint had a total volume of 100 gallons, a total weight of 877.5 lbs, volume solids of 40.0%, weight solids of 42.7%, density of 8.78 lbs/gallon, 7.0% coalescent on binder solids. Its Stormer viscosity was 94.0. The Brookfield viscosity was 4,900 cps. Its pH was 8.9.

## Example 19

This example describes the preparation of a gloss acrylic binder prepaint. It was prepared by combining the following ingredients:

Ingredients	Amounts (lbs./100 gallons)
Defoamer (Foamaster™ VL)	3.00
Binder - Acrylic Copolymer (50% solids - Tg 28° C.) (Rhoplex™ SG-10M - Rohm and Haas)	755.99
Coalescent (Texanol™)	37.80
Rheology Modifier - HEUR (Acrysol™ RM-2020-NPR - Rohm and Haas)	11.62
Base - Ammonia (28%)	0.35
Solvent - Propylene Glycol	50.00
Water	17.68

The resulting prepaint had a total volume of 100 gallons, a total weight of 876.4 lbs, volume solids of 40.0%, weight solids of 43.1%, a density of 8.76 lbs/gallon, 10.0% coalescent on binder solids. Its Stormer viscosity was 96. The Brookfield viscosity was 5,000 cps. Its pH was 8.8.

## Example 20

This example describes the preparation of a white prepaint by combining the following ingredients:

45	Ingredient	Amount (lbs./100 gallons)
Pigment - Titanium Dioxide (Ti-Pure™ R-706 - DuPont)	1001.66	
Dispersant (Tamol™ 1124 - Rohm and Haas)	20.03	
Defoamer (Drewplus™ L-475)	1.00	
Binder Acrylic (50% solids - Tg 28° C. (Rhoplex™ SG-10M - Rohm and Haas)	189.00	
Opacifier - Voided Latex Particles (Ropaque™ OP-96 - Rohm and Haas)	172.50	
Coalescent (Texanol™)	14.72	
Rheology Modifier (Acrysol™ RM-8W - Rohm and Haas)	2.00	
Base - Ammonia (28%)	1.65	
Water	200.44	

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,603.0 lbs., total PVC of 80.0%, volume solids of 50.0%, weight solids of 71.7%, a density of 16.03 lbs./gallon, 1% dispersant on pigment solids, and 10.0% coalescent on latex solids.

## Example 21

This example describes the preparation of a white pigment prepaint with pigmented vesiculated polymeric bead.

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The pigmented vesiculated polymeric bead has a particle size of 12.5 microns, approximately 7% (s/s) titanium dioxide, and a void volume of approximately 77%. The ingredients are mixed as described in Example 1 using the ingredient amounts set out below.

Ingredient	Amount (lbs./100 gallons)
Pigmented Vesiculated Polymeric Bead (Spindrift™ 25)	733.00
Dispersant (Tamol™ 1124 - Rohm and Haas)	0
Defoamer (Drewplus™ L-475)	2.00
Binder Acrylic (53.5% solids - Tg 18° C.) (Rhoplex™ ML-200 - Rohm and Haas)	154
Coalescent (Texanol™)	5.90
Rheology Modifier (Acrysol™ RM-8W - Rohm and Haas)	2.55
Water	15.89

The resulting prepaint should have a total volume of 100 gallons, total weight of 913.3 lbs, total PVC of 80.0%, volume solids of 44.0%, weight solids of 28.28%, and density of 9.13 lbs/gallon. Its Stormer viscosity should be 91 KU. Its pH should be 8.5-9.0. If not, the pH is adjusted as described in Example 7.

## Example 22.

This example describes the preparation of an exterior pigment extender prepaint by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Pigment - Nepheline Syenite (7.5μ) (Minex™ 4)	871.44
Dispersant (Tamol™ 1124 - Rohm and Haas)	8.71
Defoamer (Drewplus™ L-475)	2.00
Binder Acrylic (60.5% solids - Tg 16° C.) (Rhoplex™ AC-264 - Rohm and Haas)	154.74
Coalescent (Texanol™)	6.56
Rheology Modifier (Acrysol™ RM-8W - Rohm and Haas)	3.00
Water	326.08

The resulting prepaint should have a total volume of 100 gallons, total weight of 1,382.5 lbs., total PVC of 80.0%, volume solids of 50.0%, weight solids of 69.8%, density of 13.82 lbs./gallon, 0.5% dispersant on pigment solids, and 7.0% coalescent on latex solids.

## Example 23

This example describes the preparation of an interior pigment extender prepaint by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Pigment - Calcium Carbonate (12μ) (Omyacarb™ 12)	450.67
Pigment - Calcium Carbonate (3.2μ) (Vicron™ 15-15)	226.17
Pigment - Aluminum Silicate (1.4μ) (Optiwhite™)	183.76

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Ingredient	Amount (lbs./100 gallons)
5 Dispersant (Tamol™ 1124 - Rohm and Haas)	8.61
Defoamer (Drewplus™ L-475)	1.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES 3803)	175.09
Coalescent (Texanol™)	6.74
10 Rheology Modifier - HEUR (Acrysol™ SCT-275)	15.00
Base - Ammonia (28%)	0.87
Water	308.13

15 The resulting prepaint should have a total volume of 100 gallons, total weight of 1376.0 lbs, total PVC of 80.0%, volume solids of 50.0%, weight solids of 69.5%, density of 13.76 lbs/gallon, 0.5% dispersant on pigment solids, and 7.0% coalescent on latex solids.

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## Example 24

This example describes the preparation of a vinyl acetate/acrylic binder prepaint by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
30 Defoamer (Drewplus™ L-475)	2.00
Binder - Vinyl Acetate/Acrylic (55% solids - Tg 14° C.) (RES 3803)	875.62
Coalescent (Texanol™)	13.00
Rheology Modifier HEUR (Acrysol™ SCT-275 - Rohm and Haas)	9.29

35 The resulting prepaint should have a total volume of 100 gallons, total weight of 899.9 lbs., a total PVC of 0.0%, volume solids of 50.0%, weight solids of 53.2%, density of 8.99 lbs./gallon, and 10.0% coalescent on latex solids.

## Example 25

40 This example describes the preparation of a flat acrylic prepaint by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
50 Defoamer (Drewplus™ L-475)	8.00
Binder Acrylic (60.5% solids - Tg 16° C.) (Rhoplex™ AC-264 - Rohm and Haas)	773.67
Coalescent (Texanol™)	23.40
Rheology Modifier (HEUR) (Acrysol™ RM-8W - Rohm and Haas)	13
Base - Ammonia (28%)	0.50
Solvent - Propylene Glycol	60.00
Water	1.84

60 The resulting prepaint should have a total volume of 100 gallons, total weight of 880.4 lbs., total PVC of 0.0%, volume solids of 50.0%, weight solids of 53.2%, density of 8.80 lbs./gallon, and 5.0% coalescent on latex solids.

## Example 26

65 This example describes the preparation of a gloss acrylic binder prepaint by combining the following ingredients:

Ingredient	Amount (lbs./100 gallons)
Binder - Acrylic (50% solids - $T_g$ 28° C.) (Rhoplex™ SG-10 M- Rohm and Haas)	836.85
Coalescent (Texanol™)	41.84

The resulting prepaint should have a total volume of 100<sup>10</sup> gallons, a total weight of 878.7 lbs, total PVC of 0.0%, volume solids of 44.3%, weight solids of 47.4%, density of 8.78 lbs./gallon, and 10.0% coalescent on latex solids.

#### Example 27

This example describes the preparation of nine exterior flat latex paints of varying quality and tone using different combinations of the white pigment prepaint of Example 14, the exterior pigment extender prepaint of Example 15, the vinyl acetate-acrylic (PVA) binder prepaint of Example 17, and the flat acrylic binder prepaint of Example 18. The paints are formulated by adding the white pigment prepaint and exterior pigment extender prepaint to the binder prepaints and mixing well.

Prepaints (wt.)						
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	Exterior Extender (Ex 15)	PVA Binder (Ex 17)	Flat Acrylic Binder (Ex 18)
27-1	45.0	35.0	395.53	269.60	—	335.92
27-2	50.0	30.0	317.19	311.10	—	246.80
27-3	50.0	30.0	263.69	359.94	197.64	51.38
27-4	42.5	35.0	197.77	415.12	—	359.92
27-5	47.5	30.0	158.60	425.86	—	267.37
27-6	47.5	30.0	131.84	450.28	214.11	55.67
27-7	40.0	35.0	—	560.64	—	383.91
27-8	45.0	30.0	—	540.62	—	287.93
27-9	45.0	30.0	—	540.62	230.58	59.95

Paints 27-1, 27-4 and 27-7 are premium quality light, mid and deep tone paints; paints 27-2, 27-5 and 27-8 are first quality light, mid and deep tone paints; and paints 27-3, 27-6 and 27-9 are second quality light, mid and deep tone paints.

#### Example 28

This example describes the preparation of nine exterior satin latex paints of varying quality and tone using different combinations of the white pigment prepaint and exterior pigment extender prepaint of Examples 14 and 15, respectively, and the vinyl acetate/acrylic binder (PVA) and flat acrylic binder prepaints of Examples 17 and 18. The paints are formulated as described above.

Prepaints (wt.)						
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	Exterior Extender (Ex 15)	PVA Binder (Ex 17)	Flat Acrylic Binder (Ex 18)
28-1	35.0	35.0	395.53	129.44	—	431.90
28-2	37.0	30.0	351.59	123.51	—	353.75

-continued

#### Prepaints (wt.)

Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	Exterior Extender (Ex 15)	PVA Binder (Ex 17)	Flat Acrylic Binder (Ex 18)	Water (wt.)
28-3	40.0	26.0	263.69	175.73	228.35	59.41	292.15
28-4	32.5	36.0	197.77	287.98	—	468.92	83.47
28-5	34.5	30.0	175.75	253.98	—	374.31	208.68
28-6	37.5	26.0	131.84	270.07	242.63	63.12	292.12
28-7	30.0	36.0	—	432.50	—	493.60	83.47
28-8	32.0	30.0	—	384.44	—	394.88	208.68
28-9	35.0	26.0	—	364.42	256.87	66.86	292.15

Paints 28-1, 28-4 and 28-7 are premium quality light, mid and deep tone paints; paints 28-2, 28-5 and 28-8 are first quality light, mid and deep tone paints; and paints 28-3, 28-6 and 28-9 are second quality light, mid and deep tone paints.

#### Example 29

This example describes the preparation of nine exterior gloss latex paints of using different combinations of the white pigment and exterior extender prepaints of Examples 14 and 15 and vinyl acetate/acrylic binder (PVA) and gloss acrylic binder prepaints of Examples 17 and 19. The paints are formulated as described above.

Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	PVA Binder (Ex 17)	Gloss Acrylic Binder (Ex 19)	Water (wt.)
29-1	26.0	35.0	435.66	—	494.85	104.34
29-2	30.0	30.0	460.50	—	413.60	166.94
29-3	30.0	30.0	429.93	304.15	88.51	208.68
29-4	13.0	35.0	217.83	—	630.87	104.34
29-5	15.0	30.0	230.25	—	557.38	166.94
29-6	15.0	30.0	214.96	409.14	119.06	208.68
29-7	—	35.0	—	—	766.89	104.34
29-8	—	30.0	—	—	701.15	166.94
29-9	—	30.0	—	514.12	149.61	208.68

Paints 29-1, 29-4 and 29-7 are premium quality light, mid and deep tone paints; paints 29-2, 29-5 and 29-8 are first quality light, mid and deep tone paints; and paints 29-3, 29-6 and 29-9 are second quality light, mid and deep tone paints.

#### Example 30

This example describes the preparation of nine interior flat latex paints using different combinations of the white pigment and interior extender prepaints of Examples 14 and 16 and the vinyl acetate/acrylic (PVA) and flat acrylic binder prepaints of Examples 17 and 18. The paints are formulated as described above.

Prepaints (wt.)						
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	Exterior Extender (Ex 16)	PVA Binder (Ex 17)	Flat Acrylic Binder (Ex 18)
30-1	50.0	30.0	351.59	273.94	197.64	51.38
30-2	60.0	30.0	263.69	470.21	166.40	—
30-3	75.0	25.0	128.02	620.95	34.67	—
30-4	47.5	15.0	175.79	401.73	214.11	55.67
30-5	57.5	30.0	131.84	558.69	187.20	—
30-6	72.5	25.0	64.01	653.67	52.00	—
30-7	45.0	30.0	—	529.51	230.58	59.95
30-8	55.0	30.0	—	647.18	208.01	—
30-9	70.0	25.0	—	686.40	69.34	—
					313.02	

Paints 30-1, 30-4 and 30-7 are premium quality light, mid and deep tone paints; paints 30-2, 30-5 and 30-8 are first quality light, mid and deep tone paints; and paints 30-3, 30-6 and 30-9 are second quality light, mid and deep tone paints.

#### Example 31

This example describes the preparation of nine interior satin latex paints using the white pigment and interior extender prepaints of Examples 14 and 16 and the vinyl acetate/acrylic (PVA) and flat acrylic binder prepaints of Examples 17 and 18. The paints are formulated as described above.

Prepaints (wt.)						
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	Interior Extender (Ex 16)	PVA Binder (Ex 17)	Flat Acrylic Binder (Ex 18)
31-1	35.0	36.0	395.53	140.51	355.75	92.49
31-2	37.0	30.0	351.59	120.98	357.77	—
31-3	40.0	20.0	263.69	172.12	288.43	—
31-4	32.5	36.0	197.77	282.06	375.51	97.96
31-5	34.5	30.0	175.79	248.76	378.57	—
31-6	37.5	26.0	131.84	264.52	306.46	—
31-7	30.0	36.0	—	423.61	395.28	102.77
31-8	32.0	30.0	—	376.54	399.37	—
31-9	35.0	26.0	—	356.93	324.49	—
					292.15	

Paints 31-1, 31-4 and 31-7 are premium quality light, mid and deep tone paints; paints 31-2, 31-5 and 31-8 are first quality light, mid and deep tone paints; and paints 31-3, 31-6 and 31-9 are second quality light, mid and deep tone paints.

#### Example 32

This example describes the preparation of nine interior gloss latex paints using the white pigment prepaint of Example 14 and the vinyl acetate/acrylic (PVA) and gloss acrylic binder prepaints of Examples 17 and 19. The paints are formulated as described above.

Prepaints (wt.)						
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 14)	PVA Binder (Ex 17)	Gloss Acrylic Binder (Ex 19)	Water (wt.)
32-1	26.0	35.0	435.66	—	494.85	104.34
32-2	30.0	38.0	429.93	304.15	88.51	208.68
32-3	30.1	28.0	403.18	366.31	—	250.42
32-4	13.0	35.0	217.83	—	630.87	104.34
32-5	15.0	30.0	214.96	409.14	119.06	208.68
32-6	15.0	28.0	201.59	493.78	—	250.42
32-7	—	35.0	—	—	766.89	104.34
32-8	—	30.0	—	514.12	149.61	208.68
32-9	—	28.0	—	621.24	—	250.42

Paints 32-1, 32-4 and 32-7 are premium quality light, mid and deep tone paints; paints 32-2, 32-5 and 32-8 are first quality light, mid and deep tone paints; and paints 32-3, 32-6 and 32-9 are second quality light, mid and deep tone paints.

#### Example 33

25 This example describes the preparation of a latex paint useful for architectural coatings which can be prepared using the white pigment prepaint of Example 20, the exterior pigment extender of Example 22, and the flat acrylic binder prepaint of Example 25. The paint is formulated as described 30 above.

Prepaints (wt.)					
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 20)	Exterior Extender (Ex 21)	Flat Acrylic Binder (Ex 24)
35	35	48	331.27	294.95	475.42
40	—	—	—	—	33.39

The resulting paint should be a premium paint having a satin finish and a light tone.

#### Example 34

45 This example describes the preparation of a low solids interior flat paint using the white pigment prepaint of Example 20, the interior pigment extender of Example 23, and the vinyl acetate/acrylic (PVA) binder prepaint of Example 24.

Prepaints (wt.)					
Paint No.	PVC (%)	Volume Solids (%)	White (Ex 20)	Interior Extender (Ex 22)	PVA Binder (Ex 23)
55	75	15	107.22	294.97	16.87
60	—	—	—	—	584.31

#### Example 35

This example describes the preparation of paints using the prepaints of Examples 1 to 6. The paints were prepared by mixing the pigment prepaint(s) with the binder prepaint(s), then adding the thickeners, water and colorants and mixing well. The Stormer viscosity, ICI viscosity, and pH were the equilibrated measured values.

Part A - Exterior Flat Paints (Best and Good)

<u>Prepaint (lbs.)</u>									
Paint No.	Exterior		Flat		Thickener (lbs.)				Colorant (lbs.)
	White Pigment (Ex 1)	Extender Pigment (Ex 2)	PVA Binder (Ex 4)	Acrylic Binder (Ex 6)	Acrysol SCT-275	Acrysol RM 2020	Water (lbs.)		
35-1 <sup>a</sup>	353.86	278.01	—	306.97	10.40	14.00	149.68	—	
35-2 <sup>b</sup>	235.96	351.50	177.30	46.09	26.40	11.20	237.06	—	
35-3 <sup>a</sup>	—	516.00	—	351.00	32.68	—	146.45	162	
35-4 <sup>b</sup>	—	500.00	206.58	53.70	48.48	—	237.06	162	

<u>Measured Equilibrated Values</u>					<u>Calculated Properties</u>				
Paint No.	Stormer Viscosity (KU)	ICI Viscosity (cp)	pH	Volume <sup>a</sup> (gallons)	Weight* (lbs)	PVC (%)	Volume Solids (%)	Weight Solids (%)	Density (b/gal)
35-1 <sup>c</sup>	102	1.15	8.76	100	1112.92	45.05	35.08	50.66	11.13
35-2 <sup>d</sup>	101	0.87	8.30	100	1085.52	50.04	30.05	45.68	10.86
35-3 <sup>c</sup>	110	1.90	9.02	100	1046.13	39.94	35.00	47.92	10.46
35-4 <sup>d</sup>	121	1.80	8.70	100	1045.82	45.09	29.76	43.25	10.36

Part B - Exterior Satin Paint (Better)

<u>Prepaint (lbs.)</u>									
Paint No.	Exterior		Flat		Thickener (lbs.)				Colorant (lbs.)
	White Pigment (Ex 1)	Extender Pigment (Ex 2)	PVA Binder (Ex 4)	Acrylic Binder (Ex 6)	Acrysol SCT-275	Acrysol RM 2020	Water (lbs.)		
35-5	314.56	137.00	—	323.00	17.82	17.58	234.22	—	
<u>Measured Equilibrated Values</u>									
Paint No.	Stormer Viscosity (KU)	ICI Viscosity (cp)	pH	Volume (gallons)	Weight (lbs)	PVC (%)	Volume Solids (%)	Weight Solids (%)	Density (b/gal)
35-5	104	1.19	8.95	100.00	1044.18	36.94	29.96	43.26	10.44

Part C - Exterior Semigloss (Best and Good)

<u>Prepaint (lbs.)</u>									
Paint No.	Exterior		Gloss		Thickener (lbs.)				Colorant (lbs.)
	White Pigment (Ex 1)	Extender Pigment (Ex 2)	PVA Binder (Ex 4)	Acrylic Binder (Ex 5)	Acrysol SCT-275	Acrysol RM 2020	Water (lbs.)	Colorant (lbs.)	
35-6 <sup>a</sup>	389.40	—	—	530.37	—	15.20	98.44	—	
35-7 <sup>b</sup>	383.98	—	85.33	294.89	22.40	26.00	217.67	—	
<u>Measured Equilibrated Values</u>									
Paint No.	Stormer Viscosity (KU)	ICI Viscosity (cp)	pH	Volume (gallons)	Weight (lbs)	PVC (%)	Volume Solids (%)	Weight Solids (%)	Density (b/gal)
35-6 <sup>c</sup>	99	1.19	8.54	100.00	1033.41	26.00	35.00	46.91	10.33
35-7 <sup>d</sup>	102	1.05	8.20	100.00	1030.27	30.00	29.90	42.43	10.30

-continued

Part D - Interior Flat

Paint No.	Prepaint (lbs.)		Thickener (lbs.)					
	Interior		Flat					
	White Pigment (Ex 1)	Extender Pigment (Ex 3)	PVA Binder (Ex 4)	Acrylic Binder (Ex 5)	Acrysol SCT-275	Acrysol RM 2020	Water (lbs.)	Colorant (lbs.)
35-8 <sup>a</sup>	314.56	280.69	177.31	46.09	24.00	20.80	230.22	—
35-9	115.95	590.05	30.04	—	34.60	—	336.19	—
35-10 <sup>a</sup>	—	496.07	206.55	53.67	41.92	—	236.60	162
35-11	—	643.99	62.04	—	51.36	—	320.17	162

Paint No.	Measured Equilibrated Values				Calculated Properties				
	Stormer Viscosity (KU)	ICI Viscosity (cp)	pH	Volume (gallons)	Weight (lbs)	PVC (%)	Volume Solids (%)	Weight Solids (%)	Density (b/gal)
35-8	99	1.05	8.45	100.00	1093.67	50.00	30.00	45.88	10.94
35-9	84	0.70	8.50	100.00	1106.83	75.15	24.99	43.08	11.07
35-10	120	1.90	8.60	100.00	1034.81	45.04	29.99	43.36	10.35
35-11	108	1.88	8.80	100.00	1077.56	70.00	25.05	41.74	10.78

<sup>a</sup>Best light tone and deep tone paints<sup>b</sup>Good light tone and deep tone paints

There was 0.44% dispersant based on dry pigment and 7.48% coalescent based on dry polymer.

There was 0.46% dispersant based on dry pigment and 7.40% coalescent based on dry polymer.

There was 0.50% dispersant based on dry pigment and 7.00% coalescent based on dry polymer.

There was 0.50% dispersant based on dry pigment and 7.00% coalescent based on dry polymer.

There was 0.43% dispersant based on dry pigment and 7.43% coalescent based on dry polymer.

<sup>a</sup>Best<sup>b</sup>Good

There was a 0.40% dispersant based on dry pigment solids and a 10.00% coalescent base on dry polymer.

There was a 0.40% dispersant based on dry pigment solids and a 7.97% coalescent base on dry polymer.

<sup>a</sup>Paints 35-8 and 35-10 were best light and deep tone paints.

Paints 35-9 and 35-11 were good light and deep tone paints.

The percentage dispersant on dry pigment was 0.45%, 0.48%, 0.50%, and 0.50% for paint nos. 34-8 to 34-11, respectively. The percentages of Coalescent was 7.53%, 40.47%, 7.00% and 7.00% for paint nos. 34-8 to 34-11, respectively.

Part E - Interior Satin Paint

Paint No.	Prepaint (lbs.)		Thickener (lbs.)					
	Interior		Flat					
	White Pigment (Ex 1)	Extender Pigment (Ex 3)	PVA Binder (Ex 4)	Acrylic Binder (Ex 5)	Acrysol SCT-275	Acrysol RM 2020	Water (lbs.)	Colorant (lbs.)
35-12	314.56	138.00	319.00	—	24.96	21.40	229.76	—

The paint was a better light tone paint.

Paint No.	Measured Equilibrated Values				Calculated Properties				
	Stormer Viscosity (KU)	ICI Viscosity (cp)	pH	Volume (gallons)	Weight (lbs)	PVC (%)	Volume Solids (%)	Weight Solids (%)	Density (b/gal)
35-12	93	0.91	8.37	100.00	1047.68	37.05	29.99	43.54	10.48

The dispersant in dry pigment was 0.43%.  
The coalescent in dry polymer was 7.42%.

Part F - Semi-Gloss Paint

<u>Prepaint (lbs.)</u>								
Paint No.	Interior		Gloss		<u>Thickener (lbs.)</u>			
	White Pigment (Ex 1)	Extender Pigment (Ex 3)	PVA Binder (Ex 4)	Acrylic Binder (Ex 6)	Acrysol SCT-275	Acrysol RM 2020 NPR	Water (lbs.)	Colorant (lbs.)
35-13	383.98	—	294.89	85.33	22.40	26.00	217.67	—
35-14	359.89	—	347.58	—	28.80	28.00	255.70	—

Paint nos. 35-13 were better and good light tone paints.

<u>Measured Equilibrated Values</u>				<u>Calculated Properties</u>					
Paint No.	Stormer Viscosity (KU)	ICI Viscosity (cp)	pH	Volume (gallons)	Weight (lbs)	PVC (%)	Volume Solids (%)	Weight Solids (%)	Density (b/gal)
35-13	102	1.05	8.20	100.00	1030.27	30.01	29.91	42.43	10.30
35-14	101	1.19	7.90	100.00	1019.97	30.02	28.02	40.22	10.20

30

The dispersant was 0.40% on dry pigment for paints 35-13 and 35-14.

The coalescents were 7.97% and 7.47%, respectively for paints 35-13 and 35-14.

Example 36

This example describes the preparation of a white opacifying pigment prepaint for use in an elastomeric coating. The prepaint is prepared by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (50.5% solids, $T_g = -16^\circ C$ . Rhoplex $\oplus$ 2438 - Rohm and Haas)	177.11
Water	257.90
Dispersant (Tanol $\oplus$ 165A - Rohm and Haas)	49.24
Defoamer (Nopco NXZ)	12.44
Base - Ammonia (28%)	3.94
Coalescent (Texanol)	2.68
Rheology Modifier (Acrysol $\oplus$ SCT-275)	5.00
Pigment - Titanium Dioxide (Ti-Pure R-960 - DuPont)	1292.48

The prepaint is prepared using a high speed disperser. The water, dispersant, acrylic binder, defoamer, base, and rheology modifier are combined and mixed briefly at low speed and the dry pigment is added. After all the dry pigment is added, the mixture should be dispersed at high speed, for 15-20 minutes as is known to those skilled in the art.

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,800.80 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 76.74%, a density of 18.008 lbs./gal., 0.80% dispersant on pigment solids, and 3.0% coalescent on latex solids.

Example 37

This example describes the preparation of a white opacifying pigment prepaint containing zinc oxide for use in an

elastomeric coating. The prepaint is prepared as above by combining the following ingredients:

35

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (50.5% solids, $T_g = -16^\circ C$ . Rhoplex $\oplus$ 2438 - Rohm and Haas)	177.11
Water	278.10
Dispersant (Tanol $\oplus$ 2001 - Rohm and Haas)	26.99
Surfactant (Triton $\oplus$ X-405 - Union Carbide)	10.00
Defoamer (Nopco NXZ)	5.00
Base - Ammonia (28%)	3.94
Coalescent (Texanol)	2.68
Rheology Modifier (Acrysol $\oplus$ SCT-275)	5.00
Pigment - Zinc Oxide (XX-503 - Zinc Corporation of America)	283.26
Pigment - Titanium Dioxide (Ti-Pure R-706 - DuPont)	1133.50

50

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,925.58 lbs., a total PVC of 67.90%, a titanium dioxide PVC of 67.90%, a volume solids of 50.00%, a weight solids of 78.22%, a density of 19.2558 lbs./gal., 0.80% dispersant on pigment solids, and 3.0% coalescent on latex solids.

60

Example 38

This example describes the preparation of an extender pigment prepaint for use in an elastomeric coating. The prepaint is prepared as above by combining the following ingredients:

flexibility. The pigment is prepared using a laboratory mixer having a 45° pitch stirring blade.

Ingredient	Amount (lbs./100 gal.)
Water	295.80
Dispersant (Tamol™ 731A - Rohm and Haas)	10.82
Defoamer (Nopco NXZ)	13.36
Base - Ammonia (28%)	6.68
Coalescent (Texanol™)	1.79
Rheology Modifier (Natrosol 250 HR)	1.00
Binder Acrylic (50.5% solids, Tg = -16° C., Rhoplex™ 2438 - Rohm and Haas)	177.11
Pigment - Calcium Carbonate (Duramite™)	901.50

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,408.05 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 70.38%, a density of 14.0805 lbs./gal., 0.30% dispersant on pigment solids, and 2.0% coalescent on latex solids.

#### Example 39

This example describes the preparation of a low T<sub>g</sub> acrylic binder prepaint with good low temperature flexibility. The prepaint is prepared using a laboratory mixer having a 45° pitch stirring blade.

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (50.5% solids, Tg = -16° C., Rhoplex® 2438 - Rohm and Haas)	814.71
Defoamer (Nopco NXZ)	1.33
Rheology Modifier (Natrosol 250 HR)	5.32
Solvent - Propylene Glycol	26.62
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	8.23
Water	6.06

The resulting prepaint should have a total volume of 100 gallons, a total weight of 864.93 lbs., a volume solids of 46.00%, a weight solids of 47.57%, a density of 8.6493 lbs./gal., and 2.0% coalescent on latex solids.

#### Example 40

This example describes the preparation of a mid-range T<sub>g</sub> styrene/acrylic binder prepaint with low temperature flexibility only down to -5° C. The pigment is prepared using a laboratory mixer having a 45° pitch stirring blade.

Ingredient	Amount (lbs./100 gal.)
Binder Styrene/Acrylic (55.0% solids, Tg = -5° C., Rhoplex® 2019R - Rohm and Haas)	803.91
Defoamer (Nopco NXZ)	1.33
Rheology Modifier (Natrosol 250 HR)	5.32
Solvent - Propylene Glycol	26.62
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	8.84
Water	10.99

The resulting prepaint should have a total volume of 100 gallons, a total weight of 859.69 lbs., a volume solids of 50.00%, a weight solids of 51.43%, a density of 8.5969 lbs./gal., and 2.0% coalescent on latex solids.

#### Example 41

This example describes the preparation of a high T<sub>g</sub> (14° C.) 100% acrylic binder prepaint with poor low temperature

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (53.5% solids, Tg = 14° C., Multilobe™ 200 - Rohm and Haas)	822.40
Defoamer (Nopco NXZ)	1.33
Rheology Modifier (Natrosol 250 HR)	5.32
Solvent - Propylene Glycol	26.62
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	26.40
Water	0.36

The resulting prepaint should have a total volume of 100 gallons, a total weight of 885.11 lbs., a volume solids of 47.00%, a weight solids of 49.71%, a density of 8.8511 lbs./gal., and 6.0% coalescent on latex solids.

#### Example 42

This example describes the preparation of 11 elastomeric wall coating formulations of varying quality and mildew resistance using different combinations of the white pigment prepaints of Examples 36 and 37, the extender prepaints of Example 38, and the binder prepaints of Examples 39, 40 and 41. The paints are formulated by adding the white pigment prepaint and extender prepaint to the binder prepaints and mixing well.

Table 1: The prepaint amounts mixed together are those given below. All weights are in lbs., the total volume of each elastomeric coating is 100 gallons, formulated to 45% volume solids.

Paint	Weight of Example Prepaints							
	36	37	38	39	40	41	Water	Total
42-1	70.9	0.0	419.8	528.8	0.0	0.0	42.4	1061.9
42-2	0.0	89.3	409.9	528.8	0.0	0.0	42.4	1070.5
42-3	70.9	0.0	657.4	370.2	0.0	0.0	54.6	1153.1
42-4	0.0	89.3	647.5	370.2	0.0	0.0	54.6	1161.6
42-5	131.7	0.0	372.3	528.8	0.0	0.0	42.4	1075.2
42-6	0.0	165.9	353.9	528.8	0.0	0.0	42.4	1091.0
42-7	131.7	0.0	609.9	370.2	0.0	0.0	54.6	1166.3
42-8	0.0	165.9	591.5	370.2	0.0	0.0	54.6	1182.2
42-9	70.9	0.0	419.8	0.0	483.6	0.0	83.0	1057.3
42-10	0.0	89.3	647.5	0.0	338.5	0.0	83.0	1158.3
42-11	70.9	0.0	657.4	227.5	0.0	141.6	58.7	1014.5

TABLE 2  
The expected PVC, TiO<sub>2</sub> level, low temperature flexibility, and quality of the resulting elastomeric coatings are shown below.

Paint	PVC	ZnO presence	TiO <sub>2</sub> PVC	Flex	Quality
42-1	30	no	3.5	0° F.	medium
42-2	30	yes	3.5	0° F.	medium
42-3	45	no	3.5	0° F.	low
42-4	45	yes	3.5	0° F.	low
42-5	30	no	6.5	0° F.	high
42-6	30	yes	6.5	0° F.	high
42-7	45	no	6.5	0° F.	medium
42-8	45	yes	6.5	0° F.	medium
42-9	30	no	3.5	20° F.	medium
42-10	45	yes	3.5	20° F.	low
42-11	45	no	3.5	40° F.	poor

The elastomeric coating preparations shown above represent a range of qualities that depend upon the durability

and the flexibility at low temperature. These examples are not intended to be limiting. For instance, all the pigment and extender prepaints can be formulated with or without binders, and the binders may have a higher  $T_g$  than the one used in these examples. In addition, the extender prepaint is not meant to be limited to the use of calcium carbonate, but to show an example that could also include other commonly used extenders such as, clays, silicas, magnesium silicates, and the like.

Elastomeric coatings for use for roofs can be differentiated in the same manner as for elastomeric coatings for walls, with two additional variations, the use of functional extenders such as aluminum trihydrate to promote flame retardancy, and enhanced adhesion to specific roofing substrates. The examples that follow are intended to show the capabilities of the prepaint concept when applied to elastomeric roof coatings, and are not intended to limit.

#### Example 43

This example describes the preparation of a white pigment prepaint which is prepared by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (55.0% solids, $T_g = -29^\circ C$ . Rhoplex $\circledast$ EC-1791 - Rohm and Haas)	159.75
Water	268.95
Dispersant (Tanol $\circledast$ 165A - Rohm and Haas)	49.24
Defoamer (Nopco NXZ)	12.44
Base - Ammonia (28%)	3.94
Coalescent (Texanol)	2.64
Rheology Modifier (Acrysol $\circledast$ SCT-275)	10.00
Pigment - Titanium Dioxide (Ti-Pure R-960 - DuPont)	1292.48

The prepaint is prepared using a high speed disperser. The water, dispersant, acrylic binder, defoamer, base, and rheology modifier are combined and mixed at briefly low speed and then the dry pigment is added. After all the dry pigment is added, the mixture can be dispersed at high speed, for 15–20 minutes as is known to those skilled in the art.

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,799.45 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 76.71%, a density of 17.9945 lbs./gal., 0.80% dispersant on pigment solids, and 3.0% coalescent on latex solids.

#### Example 44

This example describes the preparation of a white opacifying prepaint for use in preparing coatings which have good adhesion to asphaltic roofing materials. The prepaint is prepared by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (55.0% solids, $T_g = -8^\circ C$ . Lipacryl $\circledast$ MB-3640 - Rohm and Haas)	160.69
Water	268.12
Dispersant (Tanol $\circledast$ 165A - Rohm and Haas)	49.24
Defoamer (Nopco NXZ)	12.44
Base - Ammonia (28%)	3.94

continued

Ingredient	Amount (lbs./100 gal.)
Coalescent (Texanol)	2.65
Rheology Modifier (Acrysol $\circledast$ SCT-275)	10.00
Pigment - Titanium Dioxide (Ti-Pure R-960 - DuPont)	1292.48

10 The prepaint is prepared using a high speed disperser, as illustrated in Example 43. The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,799.56 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 76.73%, a density of 17.9956 lbs./gal., 0.80% dispersant on pigment solids, and 3.0% coalescent on latex solids. This prepaint is designed to work best in coatings used for asphaltic substrates.

#### Example 45

20 This example describes the preparation of a white opacifying prepaint containing zinc oxide. The prepaint is prepared as above by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (55.0% solids, $T_g = -29^\circ C$ . Rhoplex $\circledast$ BC-1791 - Rohm and Haas)	159.75
Water	272.67
Dispersant (Tanol $\circledast$ 731A - Rohm and Haas)	44.09
Surfactant (Triton $\circledast$ X-405 - Union Carbide)	10.00
Defoamer (Nopco NXZ)	5.00
Base - Ammonia (28%)	3.94
Coalescent (Texanol)	2.64
Rheology Modifier (Acrysol $\circledast$ SCT-275)	12.00
Pigment - Zinc Oxide (ZKX-503 - Zinc Corporation of America)	275.47
Pigment - Titanium Dioxide (Ti-Pure R-960 - DuPont)	1102.32

40 The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,887.88 lbs., a total PVC of 80.00%, a titanium oxide PVC of 68.23%, a volume solids of 50.00%, a weight solids of 77.63%, a density of 18.8788 lbs./gal., 0.80% dispersant on pigment solids, and 3.0% coalescent on latex solids.

#### Example 46

45 This example describes the preparation of an extender pigment prepaint. The prepaint is prepared as above by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Water	310.92
Dispersant (Tanol 731A - Rohm and Haas)	10.82
Defoamer (Nopco NXZ)	13.36
Base - Ammonia (28%)	6.68
Coalescent (Texanol)	1.76
Rheology Modifier (Natrosol 2501 HR)	2.00
Binder Acrylic (55.0% solids, $T_g = -29^\circ C$ . Rhoplex $\circledast$ EC-1791 - Rohm and Haas)	159.75
Pigment - Calcium Carbonate (Duramite)	901.50

65 The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,406.78 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 70.33%, a density of 14.0678 lbs./gal., 0.30% dispersant on pigment solids, and 2.0% coalescent on latex solids.

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## Example 47

This example describes the preparation of an extender pigment prepaint for use in preparing coatings which have good adhesion to asphalt roofing materials. The prepaint is prepared as above by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Water	310.09
Dispersant (Tanol 731A - Rohm and Haas)	10.82
Defoamer (Nopco NXZ)	13.36
Base - Ammonia (28%)	6.68
Coalescent (Texanol)	1.77
Rheology Modifier (Natrosol 250 HR)	2.00
Binder Acrylic (55.0% solids, $T_g = -8^\circ C$ , Lipacryl® MB-3640 - Rohm and Haas)	160.69
Pigment - Calcium Carbonate (Duramite)	901.50

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,406.90 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 70.36%, a density of 14.0690 lbs./gal., 0.30% dispersant on pigment solids, and 2.0% coalescent on latex solids.

## Example 48

This example describes the preparation of an extender pigment prepaint using aluminum trihydrate which is known to impart flame retardant properties. It is prepared as described above by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Water	311.61
Dispersant (Tanol 731A - Rohm and Haas)	9.70
Defoamer (Nopco NXZ)	13.36
Base - Ammonia (28%)	6.68
Coalescent (Texanol)	1.76
Rheology Modifier (Natrosol 250 HR)	2.00
Binder Acrylic (55.0% solids, $T_g = -29^\circ C$ , Rhoplex® EC-1791 - Rohm and Haas)	159.75
Pigment - Aluminum Trihydrate (Solem SB-432 Huber)	807.94

45

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,312.79 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 68.24%, a density of 13.1279 lbs./gal., 0.30% dispersant on pigment solids, and 2.0% coalescent on latex solids.

## Example 49

This example describes the preparation of low  $T_g$  acrylic binder prepaint which should have with good low temperature flexibility and good adhesion to a variety of roofing substrates. The paint is prepared using a laboratory mixer having a 45% pitching blade.

55

The resulting prepaint should have a total volume of 100 gallons, a total weight of 860.52 lbs., a volume solids of 50.00%, a weight solids of 51.35%, a density of 8.6052 lbs./gal., and 2.0% coalescent on latex solids.

60

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (55.0% solids, $T_g = 29^\circ C$ , Rhoplex® EC-1791 - Rohm and Haas)	798.75
Defoamer Nopco NXZ)	1.33
Rheology Modifier (Natrosol 250 HR)	5.32

## Example 51

65 This example describes the preparation of a tan pigment prepaint with zinc oxide. The prepaint is prepared as in example 46 by combining the following ingredients.

Ingredient	Amount (lbs./100 gal.)
Solvent - Propylene Glycol	26.62
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	8.79
Water	16.45

-continued

10 The resulting prepaint should have a total volume of 100 gallons, a total weight of 859.93 lbs., a volume solids of 50.00%, a weight solids of 51.09%, a density of 8.5993 lbs./gal., and 2.0% coalescent on latex solids.

## Example 50

15 This example describes the preparation of a mid-range  $T_g$  acrylic binder prepaint which should have good adhesion to asphalt roofing materials. The prepaint is prepared using a laboratory mixer having a 45° pitch stirring blade.

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (55.0% solids, $T_g = -8^\circ C$ , Lipacryl® MB-3640 - Rohm and Haas)	803.45
Defoamer (Nopco NXZ)	1.33
Rheology Modifier (Natrosol 250 HR)	5.32
Solvent - Propylene Glycol	26.62

-continued

Ingredient	Amount (lbs./100 gal.)
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	8.84
Water	12.29

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (55.0% solids, Tg = -29° C. Rhoplex ® EC-1791 - Rohm and Haas)	143.78
Water	307.35
Dispersant (Tanol ® 731A - Rohm and Haas)	30.07
Surfactant (Triton ® X-405 - Union Carbide)	10.00
Defoamer (Nopco NXZ)	5.00
Base - Ammonia (28%)	3.94
Coalescent (Texanol)	2.37
Rheology Modifier (Acrysol ® SCT-275)	40.00
Pigment - Zinc Oxide (ZX-503 - Zinc Corporation of America)	480.33
Pigment - Tan Iron Oxide (Mapico 422)	1023.06

15

The resulting prepaint should have a total volume of 100 gallons, a total weight of 2,045.89 lbs., a total PVC of 80.00%, a volume solids of 45.00%, a weight solids of 77.35%, a density of 20.4589 lbs./gal., 0.50% dispersant on pigment solids, and 3.0% coalescent on latex solids.

The resulting prepaint should have a total volume of 100 gallons, a total weight of 1,391.11 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 69.92%, a density of 13.9111 lbs./gal., 0.75% dispersant on pigment solids, and 2.0% coalescent on latex solids.

#### Example 52

This example describes the preparation of an extender pigment prepaint using crystalline silica. Silica extenders are known to provide good durability and abrasion resistance. The prepaint is prepared as above by combining the following ingredients:

Ingredient	Amount (lbs./100 gal.)
Water	296.22
Dispersant (Tanol ® 731A - Rohm and Haas)	26.54
Defoamer (Nopco NXZ)	13.36
Base - Ammonia (28%)	6.68
Coalescent (Texanol)	1.76
Thickener (Natrosol 250 HR)	2.00
Binder Acrylic (55.0% solids, Tg = -29° C. Rhoplex ® EC-1791 - Rohm and Haas)	159.75
Silica Extender (Silver Bond B)	884.81

30 This example describes the preparation of 15 elastomeric roof coating formulations of varying quality, flexibility, adhesion and flame retardancy. The coatings are formulated using different combinations of the white prepaints of Examples 43, 44, and 45, the non-white pigment prepaint of Example 16, the extender prepaints of Examples 46, 47, 48, and 52 and the binder prepaints of Example 40, 49 and 50. The paints are formulated by adding the pigment prepaint and extender prepaint to the binder prepaints and mixing well. The amounts mixed are those cited below. All weights are in lbs., and the total volume of each elastomeric coating is 100 gallons. The volume solids is 45%.

#### Example 53

Paint	Weight of example prepaints											Water	Total
	43	44	45	51	46	47	48	52	40	49	50		
53-1	70.9	—	—	—	419.4	—	—	—	—	483.7	—	83	1057.0
53-2	—	—	87.2	—	409.8	—	—	—	—	483.7	—	83	1063.7
53-3	70.9	—	—	—	656.8	—	—	—	—	338.6	—	83	1149.2
53-4	—	—	87.2	—	647.2	—	—	—	—	338.6	—	83	1156.0
53-5	131.6	—	—	—	371.9	—	—	—	—	483.7	—	83	1070.2
53-6	—	—	161.9	—	354.2	—	—	—	—	483.7	—	83	1082.7
53-7	131.6	—	—	—	609.3	—	—	—	—	338.6	—	83	1162.5
53-8	—	—	161.9	—	591.6	—	—	—	—	338.6	—	83	1175.0
53-9	70.9	—	—	—	—	—	391.4	—	—	483.7	—	83	1028.9
53-10	—	—	88.9	—	—	—	647.8	—	—	338.5	—	83	1158.2
53-11	91.1	—	—	—	403.6	—	—	—	—	483.6	—	83	1061.2
53-12	—	—	112.1	—	628.7	—	—	—	—	338.5	—	83	1162.2
53-13	—	131.6	—	—	—	530.2	—	—	—	—	387.2	83	1132.1
53-14	131.6	—	—	—	530.2	—	—	—	—	387.2	—	83	1132.0
53-15	—	—	—	179.0	—	—	—	548.0	—	368.0	—	76	1171.0

The expected PVC, TiO<sub>2</sub> level, low temperature flexibility, extender type, and presence of special adhesion, and quality of the resulting elastomeric coating mixtures are shown in Table 3

Paint	PVC	ZnO	TiO <sub>2</sub>	PVC	Color	Extender	Flex Temp	Special adhesion	Quality
53-1	30	no	3.5		white	CaCO <sub>3</sub>	-15° F.	variety	medium
53-2	30	yes	3.5		white	CaCO <sub>3</sub>	-15° F.	variety	medium
53-4 3	45	no	3.5		white	CaCO <sub>3</sub>	15° F.	variety	low
53-4	45	yes	3.5		white	CaCO <sub>3</sub>	-15° F.	variety	low
53-5	30	no	6.5		white	CaCO <sub>3</sub>	-15° F.	variety	high
53-6	30	yes	6.5		white	CaCO <sub>3</sub>	-15° F.	variety	high
53-7	45	no	6.5		white	CaCO <sub>3</sub>	-15° F. 15° F.	variety	medium
53-8	45	yes	6.5		white	CaCO <sub>3</sub>	-15° F.	variety	medium
53-9	30	no	3.5		white	ATH	-15° F.	variety	medium
53-10	45	yes	3.5		white	ATH	-15° F.	variety	low
53-11	30	no	4.5		white	CaCO <sub>3</sub>	20° F.	variety	medium
53-12	45	yes	4.5		white	CaCO <sub>3</sub>	20° F.	variety	low
53-13	40	no	6.5		white	CaCO <sub>3</sub>	20° F.	asphalt	medium
53-14	40	no	6.5		white	CaCO <sub>3</sub>	20° F.	asphalt blend	medium
53-15	42	yes	0		tan	silica	-15° F.	variety	medium

The elastomeric coating preparations shown above represent a range of qualities that depend upon the durability and the flexibility of the coating at low temperature. Different extender prepaints are used to promote flame retardancy in the dried coatings. Included are prepaints prepared using dry ground colorants and no TiO<sub>2</sub> to develop tinted paints. These examples are not intended to be limiting. For instance, all the pigment and extender prepaints can be formulated with or without binders, and the binders may have a higher T<sub>g</sub> than the one used in the our example. In addition, the extender prepaint is not meant to limit use to calcium carbonate, but to show an example that could also include other commonly used extenders such as, clays, silicas, magnesium silicates, etc.

#### Example 54

This example describes the preparation of a white pigment prepaint/preformulated component.

Ingredient	Amount (lbs./100 gal.)
Water	275.83
Solvent - Propylene Glycol	50.00
Dispersant (Tamol # 731A - Rohm and Haas)	26.71
Defoamer (Nopco NXZ)	1.50
Surfactant (Triton CF-10)	1.00
Pigment - Titanium Dioxide (Ti-Pure R-902 - DuPont)	1335.56
Base (Ammonia - 28%)	4.00
Defoamer (Nopco NXZ)	1.50
Thickener (Acrysol # RM-2020 NPR - Rohm and Haas)	50.00
Water	93.45

The water, glycol, defoamer, dispersant and surfactant are combined and mixed briefly at low speed. The dry pigment is then added. After all the dry pigment is added, the mixture is mixed at high shear for 15-20 minutes as is known to those skilled in the art.

The resulting white pigment prepaint/preformulation should have a total volume of 100 gallons, a total weight of 1,839.55 lbs., a total PVC of 100.00%, a volume solids of 40.12%, a weight solids of 72.60%, a density of 18.4495 lbs./gal., and 0.50% dispersant on pigment solids.

#### Example 55

This example describes the preparation of a small particle size extender prepaint/preformulated component:

Ingredient	(lbs./100 gal.)
Binder Acrylic (46.5% solids, Tg = 17° C.	201.32
Rhoplex # EI-2000 - Rohm and Haas)	
Solvent - Propylene Glycol	5.00
Dispersant (Tamol # 731A - Rohm and Haas)	10.42
Defoamer (Nopco NXZ)	2.00
Thickener #1 (Attagel 50)	27.96
Small particle size extender (Minex 4)	840.53
Coleoscent (Texanol)	3.28
Base (Ammonia - 28%)	2.00
Water	283.42
Thickener #2 (Acrysol # ASE-60 - Rohm and Haas)	4.00

The water, acrylic binder, defoamer, base, and glycol are combined and mixed briefly at low speed. The dry extender is then added. After all the dry extender is added, the mixture is mixed at high shear for 15-20 minutes as is known to those skilled in the art.

The resulting small particle size extender prepaint/preformulation should have a total volume of 100 gallons, a total weight of 1,379.93 lbs., a total PVC of 80.00%, a volume solids of 50.00%, a weight solids of 69.72%, a density of 13.7993 lbs./gal., 0.30% dispersant on pigment solids, and 3.50% coalescent on latex solids.

#### Example 56

This example describes the preparation of a binder prepaint/preformulation. It is prepared using a laboratory mixer having a 45° pitch stirring blade.

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (46.5% solids, Tg = 17° C.	805.28
Rhoplex # EI-2000 - Rohm and Haas)	
Defoamer (Nopco NXZ)	1.33
Thickener (Acrysol # ASE-60 - Rohm and Haas)	20.00
Solvent - Propylene Glycol	10.00

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Ingredient	Amount (lbs./100 gal.)
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	13.11
Water	21.92

The resulting binder prepaint/preformulation package should have a total volume of 100 gallons, a total weight of 874.31 lbs., a volume solids of 40.00%, a weight solids of 42.83%, a density of 8.7431 lbs./gal., and 3.50% coalescent on latex solids.

## Example 57

This example describes the preparation of binder prepaint/preformulation for good low temperature flexibility. It is prepared using a laboratory mixer having a 45° pitch stirring blade.

Ingredient	Amount (lbs./100 gal.)
Binder Acrylic (61% solids, Tg = -29° C.)	584.20
Rhoplex ® EC-2848 - Rohm and Haas)	
Defoamer (Nopco NXZ)	1.33
Thickener (Acrysol ® ASE-60 - Rohm and Haas)	20.00
Solvent - Propylene Glycol	10.00
Base - Ammonia (28%)	2.66
Coalescent (Texanol)	12.47
Water	226.92

The resulting preformulated binder package should have a total volume of 100 gallons, a total weight of 857.59 lbs., a volume solids of 40.00%, a weight solids of 41.55%, a density of 8.5759 lbs./gal., and 3.50% coalescent on latex solids.

## Example 58

This example describes a small particle size aggregate for use in giving the aggregate finish a fine texture.

Ingredient	Amount (lbs./100 gal.)
Sand - Small Particle Size (Sand #90)	2,211.18

The resulting preformulated aggregate package should have a total volume of 100 gallons, a total weight of

Paint	Weight of Example Prepaints							
	55	56	57	58	59	54	Water	Total
60-1	64.72	429.09		995.56		0.00	10.03	1499.40
60-2	41.60	432.75		995.56		30.90	6.55	1507.11
60-3	6.93	438.24		995.56		77.26	1.34	1518.66
60-4	180.29	337.56		995.56		0.00	27.41	1540.82
60-5	157.17	341.22		995.56		30.90	23.93	1548.52
60-6	122.50	346.71		995.56		77.26	18.72	1560.08
60-7	295.86	246.03		995.56		0.00	44.79	1582.24
60-8	272.74	249.69		995.56		30.90	41.31	1589.94
60-9	238.07	255.18		995.56		77.26	36.10	1601.50
60-10	122.50		340.08	995.56		77.26	18.72	1553.45
60-11	64.72	429.09			995.56	0.00	10.03	1499.40
60-12	41.60	432.75			995.56	30.90	6.55	1507.11

-continued

Paint	Weight of Example Prepaints							Total
	55	56	57	58	59	54	Water	
60-13	6.93	438.24			995.56	77.26	1.34	1518.66
60-14	180.29	337.56			995.56	0.00	27.41	1540.82
60-15	157.17	341.22			995.56	30.90	23.93	1548.52
60-16	122.50	346.71			995.56	77.26	18.72	1560.08
60-17	295.86	246.03			995.56	0.00	44.79	1582.24
60-18	272.74	249.69			995.56	30.90	41.31	1589.94
60-19	238.07	255.18			995.56	77.26	36.10	1601.50

The PVC, TiO<sub>2</sub> level, expected color intensity, texture, and low temperature flexibility of the resulting aggregate finish coating formulations shown below.

Paint	PVC	TiO <sub>2</sub>	PVC	Texture	Flex	Color tone	Quality	20
60-1	70	0		fine	40° F.	deep	high	
60-2	70	1		fine	40° F.	mid-tone	high	
60-3	70	2.5		fine	40° F.	pastel	high	
60-4	75	0		fine	40° F.	deep	medium	25
60-5	75	1		fine	40° F.	mid-tone	medium	
60-6	75	2.5		fine	40° F.	pastel	medium	
60-7	80	0		fine	40° F.	deep	low	
60-8	80	1		fine	40° F.	mid-tone	low	
60-9	80	2.5		fine	40° F.	pastel	low	
60-10	75	2.5		fine	0° F.	pastel	medium	30
60-11	70	0		coarse	40° F.	deep	high	
60-12	70	1		coarse	40° F.	mid-tone	high	
60-13	70	2.5		coarse	40° F.	pastel	high	
60-14	75	0		coarse	40° F.	deep	medium	
60-15	75	1		coarse	40° F.	mid-tone	medium	
60-16	75	2.5		coarse	40° F.	pastel	medium	
60-17	80	0		coarse	40° F.	deep	low	35
60-18	80	1		coarse	40° F.	mid-tone	low	
60-19	80	2.5		coarse	40° F.	pastel	low	

The aggregate finish coatings shown above represent a range of qualities, textures, and coloring abilities that depend upon the PVC, TiO<sub>2</sub> level, and particle size ratio of the large particle size extender. These formulations are not intended to be limited by the example. For instance, all the extender prepaints/preformulation could be formulated without binder. In addition, the extender prepaint/preformulation is not meant to be limited to the use of nepheline syenite, but to show an example that includes other commonly used extenders such as, clays, silicas, magnesium silicates, calcium carbonates, etc. The TiO<sub>2</sub> slurry can be added to the extender prepaint/preformulation.

#### Example 61

The following prepaints should provide a range of coatings for wood, including coatings that contain an opacifying pigment ("pigmented coatings") and coatings that do not contain an opacifying pigment or extenders on a pigment ("clear coatings"):

Binder Prepaint 1 is made by adding 7979 g of Rhoplex CL-104 binder to a vessel. With good agitation, 800 g

of ethylene glycol monobutyl ether, 240 g of dipropylene glycol monobutyl ether, and 1800 g of water are then added.

Binder Prepaint 2 is made by adding 6636 g of Rhoplex CL-105 binder to a vessel. With good agitation, 800 g of ethylene glycol monobutyl ether, 240 g of dipropylene glycol monobutyl ether and 1800 g of water are then added.

Binder Prepaint 3 is made by adding 760 g of RoShield 3188 binder to a vessel. With good agitation, 400 g of ethylene glycol monobutyl ether, 120 g of dipropylene glycol monobutyl ether, 900 g of water, and 100 g of Paraplex™ WP-1 poly(propylene oxide), monocresyl ether (Rohm and Haas Company, Philadelphia, Pa.) are then added.

Additive Prepaint 1 is made by blending, under agitation, 70 g of Tego Foamex 805 defoamer, 30 g of Tego Glide™ 410 (50% in Dowanol DPM solvent) wax (Tego Chemie Service), 30 g of Surfynol™ 104DPM surfactant, 25 g of Acrysol™ RM-825 HASE thickener, and 200 g of Michem Emulsion 39235.

Titanium dioxide prepaint is made in a Cowles mixer as follows:

Grind	Weight (pounds)	Volume (gallons)
Water	282.96	33.90
Tamol 731™ dispersant	58.51	6.35
Triton™ CF-10 surfactant	2.19	0.25
Kathon™ LX 1.5% biocide	2.19	0.26
Ti-Pure™ R-706 titanium dioxide	1462.80	43.81
Letdown		
Ammonia (28%)	0.66	0.09
Acrysol™ RM-2020 NPF HEUR thickener	54.76	6.29
Totals	1939.64	100.00

All quantities in grams	Coatings for Board												Thermoset Coat-	
	General Purpose Topcoats-for Wood						Solvent Resistant-Topcoats for Wood							
	A gloss	B flat	C DIY gloss	D DIY flat	E white gloss	F gloss	G flat	H DIY gloss	I DIY flat	J white gloss	K gloss	L flat	M wiping stain	high build stain
Binder	10,810	10,810	10,810	10,810	7000	—	—	—	—	—	—	—	—	—
Prepaint 1	—	—	—	—	—	—	—	—	—	—	9476	9476	6120	6120
Binder	—	—	—	—	—	9200	9200	9200	9200	6550	—	—	—	—
Prepaint 2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Binder	—	—	—	—	—	—	—	—	—	—	—	—	—	3945
Prepaint 3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Binder	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rhoplex	—	—	—	—	—	—	—	—	—	—	—	—	—	—
AC-1024	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Additive	896	896	800	800	258	800	800	800	800	258	200	200	—	1700
Prepaint 1	—	—	—	—	1520	—	—	—	1520	—	—	—	—	1192
TiO <sub>2</sub>	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Prepaint	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Flatting Agent	—	120	—	120	—	—	120	—	120	—	—	120	—	—
Sylloid™ 7000	—	—	—	—	—	—	—	—	—	—	—	—	772	772
Predispersed Pigment	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Aquasperse	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Burnt Umber	—	—	—	—	—	—	—	—	—	—	—	—	258	258
877-1314	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Coalescent	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Propylene Glycol	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Water	—	—	—	—	—	—	—	—	—	—	—	—	2573	2573
Coalescent	—	—	400	400	—	—	—	300	300	—	—	—	—	983
Hexyl Carbitol	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Thickener	—	—	180	180	—	—	—	120	120	—	—	—	86	160
Acrysol™ RM-2020	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NPR	—	—	—	—	—	—	—	—	—	—	—	—	—	—

AC-1024, White, Thermoset Formulation - used with urea formaldehyde resin at 1973 g on total formulation  
These formulations can also be used as pigmented and clears on hardboard, MDF, plywood, oriented strand board.

### Example 62

The following prepaints are prepared and used for formulating a range of coatings for metal substrates that would be typical for maintenance or original equipment manufacturing applications:

Ingredient	Prepaint Formulas (pounds/100 gallons)				
	TiO <sub>2</sub> Prepaint	Extender Prepaint 1	Extender Prepaint 2	Extender Prepaint 3	Binder Prepaint
Dowanol™ DPM ester solvent	116.9	79.15	98.0	82.2	—
Water	227.3	302.8	190.1	314.3	—
Tamol™ 165A dispersant	64.95	43.97	54.19	45.64	—
Triton™ CF-10 surfactant	6.5	4.4	5.5	4.6	—
Tegofosmex™ 1488 defoamer	9.7	6.6	8.3	6.9	—
Ti-Pure™ R-706 TiO <sub>2</sub>	1266.4	—	—	—	—
2610 Lo Micron™ talc	—	857.5	—	—	—
Albaglos™ CaCO <sub>3</sub>	—	—	1062.6	—	—
Halox™ SZP-391 reactive pigment (Halox, Inc., Hammond,	—	—	—	889.9	—

-continued

Ingredient	Prepaint Formulas (pounds/100 gallons)				
	TiO <sub>2</sub> Prepaint	Extender Prepaint 1	Extender Prepaint 2	Extender Prepaint 3	Binder Prepaint
<b>IN</b>					
Ammonia 15%	2.8	1.9	2.4	1.9	—
Water	32.5	21.9	27.5	22.8	31.45
Kathon™ LX biocide	2.1	1.4	1.6	1.5	—
Acrysol™ RM-2020 NPF	56.1	56.1	56.1	—	—
HEUR thickener	—	—	—	—	—
Natrasol™ 250 GR (4%)	—	—	—	58.3	—
HEC thickener	—	—	—	—	—
Maincote™ HG-54D binder	—	—	—	—	754.8
Texanol™ coalescent	—	—	—	—	47.17
15% sodium nitrite	—	—	—	—	10.48
Ammonia 15%	—	—	—	—	5.24
Acrysol™ RM-8W HASE thickener	—	—	—	—	2.62

pH = 8.5-9

Viscosity 90-110 KU

Hegmen grinds in the range specific for that grade of pigment.

The above prepaints may be combined to form the following range of coatings for metals:						
Product Components	High PVC white Primer % by weight	Gloss white % by weight	Low gloss white % by weight	Low gloss Clear Top % by weight	Clear Topcoat % by weight	
TiO <sub>2</sub> Prepaint	10.1	13	12.5	—	—	35
Extender Prepaint 1	5.4	—	—	—	—	
Extender Prepaint 2	6.1	—	4.2	2.9	—	
Extender Prepaint 3	10.8	—	—	—	—	
Binder Prepaint	57.6	87	83.3	97.1	100	
PVC	31.89	17.82	13.98	3.37	—	
Solids - volume	34.67	35.56	35.41	35.19	35.02	40
Solids - weight	48.31	46.01	44.96	38.11	36.78	

## Example 63

A line of graphic art inks can be produced from a limited set of blended raw materials ("preinks" or "prepaints"). The prepaints are prepared as follow:

Prepaint 1 ("Hard Binder Prepaint") is prepared by adding 94 parts of Lucidene 370 polymer (Rohm and Haas Company) to a vessel. With good agitation 5 parts of Luciwax 37 wax (Rohm and Haas Company) and 1 part of a defoamer are added.

Prepaint 2 ("Mid Tg Binder Prepaint") is prepared by adding 94 parts Lucidene 615 polymer (Rohm and Haas Company) to a vessel. With good agitation 5 parts

25 of Luciwax 37 wax (Rohm and Haas Company) and 1 part of a defoamer are added.

Prepaint 3 ("Soft Binder Prepaint") is prepared by adding 89 parts of Lucidene 605 polymer (Rohm and Haas Company) to a vessel. With good agitation 5 parts of Luciwax 37 wax (Rohm and Haas Co), 1 part of a defoamer, and 5 parts isopropyl alcohol are added.

Prepaint 4 ("Alkali Soluble Resin Additive Prepaint") is Morcyl 132 resin (Rohm and Haas Company), used as supplied at 32% solids and pH 8.5

Prepaint 5 ("Gloss Additive Prepaint") is Morcyl 350 resin (Rohm and Haas Company) used as supplied at 50% solids and pH 9.0.

Prepaint 6 ("Wax Additive Prepaint") is a Michem Lube 743 wax (Michelman, Inc.) used as supplied at 32% solids and pH 7.

Color is added to the inks using pigment dispersions, such as SunFlexiverse Dispersion (Sun Chemical Co) supplied at about 40% solids, in a plurality of colors.

45 The line of graphic arts inks is described in the table below. Each product is prepared by blending the indicated materials (as weight in grams) with good agitation. The final viscosity is adjusted as desired with additional water and or isopropyl alcohol. Where a range of materials to blend is indicated, a range of properties in the final product can be obtained. For example, using the highest level of Prepaint 3 in the ink for freezer bags will result in better low temperature crinkle resistance. Using the higher level of Prepaint 4 in most inks will result in better transfer on the printing press.

Ink Product	Binder Prepaint 1	Binder Prepaint 2	Binder Prepaint 3	Additive Prepaint 4	Additive Prepaint 5	Additive Prepaint 6	Pigment Dispersion
Giftwrap Paper	55-65	—	—	10-20	—	—	25-30
Corrugated Box	55-65	—	—	10-20	—	4-6	25-30
Newsprint	65-75	—	—	—	—	—	30
Paperboard	55-65	—	—	—	10-20	—	25-30
Labels	28-33	28-33	—	10-20	—	—	25-30

## -continued

Freezer Bags	—	—	55-65	10-20	—	—	25-30
Store Bags	—	—	55-65	—	10-20	—	25-30
Metal Film	—	28-33	28-33	—	—	—	25
Foil	—	28-33	28-33	—	10-20	—	25-30
General Purpose Overprint	—	80	—	15-25	—	—	—
High Gloss Overprint	35-45	—	35-45	—	20	—	—
Water Resistant Overprint	—	35-45	35-45	10-20	—	—	—
Rub Resistant Overprint	—	75-85	—	20	—	4-6	—
High Slip Angle Overprint	—	80	—	15-25	—	—	—

Supplier Information

Material Name	Material Type	Supplier
Tamol™ 1124	Dispersant	Rohm and Haas Company (Philadelphia, PA)
Tamol™ 1254	Dispersant	Rohm and Haas Company (Philadelphia, PA)
Tamol™ 731	Dispersant	Rohm and Haas Company (Philadelphia, PA)
Acrysol™ DR-3	HASE Thickener/Rheology Modifier	Rohm and Haas Company (Philadelphia, PA)
Acrysol™ RM-2020 NPR	HEUR Thickener/Rheology Modifier	Rohm and Haas Company (Philadelphia, PA)
Acrysol™ RM-8W	HEUR Thickener/Rheology Modifier	Rohm and Haas Company (Philadelphia, PA)
Acrysol™ RM-825	HEUR Thickener/Rheology Modifier	Rohm and Haas Company (Philadelphia, PA)
Rhoplex™ Multilobe 200	Emulsion Polymer Binder	Rohm and Haas Company (Philadelphia, PA)
Rhoplex™ SG-10M	Emulsion Polymer Binder	Rohm and Haas Company (Philadelphia, PA)
RES 3083	Emulsion Polymer Binder	Rohm and Haas Company (Philadelphia, PA)
Kathon™ LX 1.5%	Biocide	Rohm and Haas Company (Philadelphia, PA)
Triton™ CF-10	Surfactant	Union Carbide Corporation (Danbury, CT)
Foamaster™ VL	Defoamer	Henkel Corporation (King of Prussia, PA)
Drewplus™ L-475	Defoamer	Drew Chemical Corporation (Kearny, NJ)
Ti-Pure™ R-746	Titanium Dioxide	E.I. DuPont de Nemours and Co., Inc. (Wilmington, DE)
Ti-Pure™ R-706	Titanium Dioxide	E.I. DuPont de Nemours and Co., Inc. (Wilmington, DE)
Ti-Pure™ R-900	Titanium Dioxide	E.I. DuPont de Nemours and Co., Inc. (Wilmington, DE)
Ti-Pure™ R-902	Titanium Dioxide	E.I. DuPont de Nemours and Co., Inc. (Wilmington, DE)
Minex™ 4	Mineral Extender	Inimin Corp. (Dividing Creek, NJ)
Optiwhite™	Clay Extender	Burgess Pigment (Sandersville, GA)
Snowflake™	Calcium Carbonate Extender	ECC International Imerys (Sylacauga, AL)
Vicron™ 15-15	Calcium Carbonate Extender	Pfizer (New York, NY)
Omyacarb™	Calcium Carbonate Extender	Omya (Proctor, VT)
Texanol™	Coalescent	Eastman Chemical (Kings Port, TN)

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## What is claimed:

1. A set of different, but mutually compatible fluid prepaints, sufficient to form at least one paint line, which set comprises:

- (i) at least one opacifying prepaint comprising at least one opacifying pigment;
- (ii) at least one extender prepaint comprising at least one extender pigment; and
- (iii) at least one binder prepaint comprising at least one latex polymeric binder.

2. The set of prepaints of claim 1, wherein the number of prepaints is from 3 to 15.

3. The set of prepaints of claim 1, wherein the opacifying prepaint further comprises at least one particulate polymeric binder adsorbed onto the opacifying pigment.

4. The set of prepaints of claim 1, wherein the extender prepaint further comprises at least one particulate polymeric binder adsorbed onto the extender pigment.

5. A method of forming at least one paint line, comprising the steps of:

(a) providing a set of different, but mutually compatible, fluid prepaints, comprising:

- (i) at least one opacifying prepaint, comprising at least one opacifying pigment;

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- ii) at least one extender prepaint comprising at least one extender pigment; and
- (iii) at least one binder prepaint comprising at least one latex polymeric binder; and
- (b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the paint line.

6. A method of forming a range of paints, the range comprising at least two paint lines, which method comprises the steps of:

- (a) providing a set of different, but mutually compatible, fluid prepaints sufficient to formulate at least two paint lines, which set comprises:
  - (i) at least one opacifying prepaint comprising at least one opacifying pigment;
  - (ii) at least one extender prepaint comprising at least one extender pigment;
  - (iii) at least one binder prepaint comprising at least one latex polymeric binder; and
  - (iv) at least one additional, different opacifying, extender, or binder prepaint selected from the group consisting of (i), (ii), and (iii); and
- (b) dispensing a predetermined amount of each of the prepaints into containers or applicator(s) to form the range of paints.

7. The method of claim 5, further comprising the step of mixing the prepaint before, while, or after they are dispensed into the containers.

8. The method of claim 5, further comprising the step of mixing the prepaint before or while they are dispensed into the applicator(s).

9. The method of claim 5, further comprising the step of adjusting the viscosity of the prepaints before, while, or after they are into the containers.

10. The method of claim 5, further comprising the step of adjusting the viscosity of the dispensed prepaints before or while they are dispensed into the applicator(s).

11. The method of claim 5, further comprising the step of adding at least one additive that enhances application or final performance of the paint.

12. The method of claim 11, wherein the additive is an aggregate material.

13. The method of claim 11, wherein the additive is a thickener.

14. The method of claim 5, further comprising the step of adding at least one colorant to the prepaints.

15. The method of claim 5, wherein the opacifying prepaint further comprises at least one particulate polymeric binder absorbed onto the opacifying pigment.

16. The method of claim 5, wherein the extender prepaint further comprises at least one particulate polymeric binder absorbed onto the extender pigment.

17. The method of claim 5, wherein the method is carried out at a paint manufacturing facility.

18. The method of claim 5, wherein the number of prepaints is from 4 to 15.

19. A fluid opacifying prepaint useful for formulating a one pack, pigmented latex paint having a volume solids content of about 30% to about 70% and a Stormer viscosity of about 50 to about 250 KU, which prepaint contains other paint ingredients, which prepaint consists essentially of:

- (i) at least one opacifying pigment,
- (ii) at least one dispersant,
- (iii) at least one thickener, and
- (iv) water;

wherein the dispersant(s) and the thickener(s) are mutually compatible with the pigment(s) and with the other paint ingredients.

20. The prepaint of claim 19, wherein the volume solids content is about 35% to about 50% and the Stormer viscosity is about 60 to about 150 KU.

21. A fluid white opacifying prepaint having a volume solids content of about 30% to about 70%, a PVC of about 35% to about 100%, and a Stormer viscosity of about 50 to about 250 KU, useful for formulating a one pack, pigmented latex paint containing other paint ingredients, which prepaint consists essentially of:

- (i) at least one opacifying pigment,
- (ii) at least one dispersant,
- (iii) at least one thickener,
- (iv) at least one film-forming or non-film-forming polymer, and
- (v) water, wherein the dispersant(s), the thickener(s), and the polymer(s) are compatible with the pigment(s) and with the other paint ingredients and wherein the prepaint is stable to sedimentation.

22. The prepaint of claim 21, wherein the volume solids content is about 35% to about 50%, the PVC is about 50 to about 100%, and the Stormer viscosity is about 60 to about 150 KU.

23. The prepaint of claim 21, wherein the polymer is adsorbed onto the opacifying pigment.

24. The prepaint of claim 19 or 21, wherein the opacifying pigment is a material selected from the group consisting of titanium dioxide, zinc oxide, lead oxide, a synthetic polymer pigment, and mixtures thereof.

25. The prepaint of claim 19 or 21, wherein the opacifying pigment is rutile titanium dioxide.

26. The prepaint of claim 24, wherein the synthetic polymer pigment is voided latex polymer particles.

27. The prepaint of claim 19 or 21, wherein the dispersant is a selected from the group consisting of 2-amino-2-methyl-1-propanol; dimethylaminoethanol; potassium tripolyphosphate; trisodium polyphosphate; citric acid; polyacrylic acid; diolefin/maleic anhydride adducts; hydrophobically-modified polyacrylic acid, hydrophilically-modified polyacrylic acid, and salts thereof; and mixtures thereof.

28. The prepaint of claim 19 or 21, wherein the thickener is a selected from the group consisting of an alkali-soluble or alkali-swellable emulsion (ASE), a hydrophobically-modified, alkali-soluble emulsion (HASE), a hydrophobically-modified ethylene oxide-urethane polymer (HEUR), a cellulosic, a hydrophobically-modified cellulosic, a hydrophobically-modified polyacrylamide, a polyvinyl alcohol, a fumed silica, an attapulgite clay, a titanate chelating agent, and mixtures thereof.

29. The prepaint of claim 21, wherein the polymer is selected from the group consisting of acrylic, polyvinyl acetate, styrene-acrylic, styrene-butadiene, vinyl acetate-acrylic, ethylene-vinyl acetate, vinyl acetate-vinyl versatate, vinyl acetate-vinyl maleate, vinyl acetate-vinyl chloride-acrylic, ethylene-vinyl acetate-acrylic polymers and mixtures thereof and wherein the polymer further comprises up to about 10% by weight of the polymer of a monomer selected from the group consisting of a functional monomer, a co-monomer, and combinations thereof.

30. The prepaint of claim 19 or 21, further consisting essentially of at least one additive selected from the group consisting of an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide, and an antifreeze agent, with the additive being present in an amount of less than about 10% by weight, based on the total weight of the prepaint.

31. A fluid pigment extender prepaint, useful for formulating a one pack, pigmented latex paint containing other paint ingredients, which prepaint consists essentially of

- (i) at least one mineral extender having a volume solids content of about 30% to about 70%, a PVC of about 35% to about 100%, and a Stormer viscosity of about 50 to about 250 KU;
- (ii) at least one thickener;
- (iii) water, and
- (iv) an optional polymeric binder, wherein the prepaint ingredients are compatible with each other and with the ingredients of the paint.

32. A set of two different, but mutually compatible binder prepaints useful for formulating a latex paint, which set comprises:

- (a) the opacifying prepaint of claim 19 or 21; and
- (b) a latex polymeric binder prepaint having volume solids content of about 25% to about 70% or a Brookfield viscosity of less than about 100,000 centipoise at a shear rate of 1.25 reciprocal seconds, which prepaint consists essentially of a water-borne latex polymeric binder having a Tg of about -430° C. to about 70° C. and water;

wherein the prepaint ingredients are mutually compatible with each other and with the ingredients of the other prepaint in the set.

33. The set of prepaints of claim 32, wherein the binder prepaint has a volume solids content of about 30 to about 65% and a Brookfield viscosity of about 100 to about 50,000 centipoise at a shear rate of 1.25 reciprocal seconds, and consists essentially of a water-borne polymeric binder having a Tg of about -10 to about 60° C.

34. The set of prepaints of claim 32, wherein the binder prepaint further consists essentially of at least one additive selected from the group consisting of an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide, and antifreeze agent, the additive being present in an amount of less than about 10% by weight, based on the total weight of the prepaint.

35. A set of three different, but mutually compatible, fluid prepaints, useful for formulating a latex paint, which set comprises:

- (a) the set of prepaints of claim 32 wherein the extender prepaint has a volume solids content of about 30% to about 70%, a PVC of about 35% to about 100%, and a Stormer viscosity of about 50 to about 250 KU; and
- (b) a fluid pigment extender prepaint which consists essentially of:

  - (i) at least one mineral extender,
  - (ii) at least one thickener,
  - (iii) water, and
  - (iv) optionally a polymeric binder.

36. The set of prepaints of claim 35, wherein the extender prepaint has a volume solids content of about 35% to about 65%, a PVC of about 40% to about 100% and a Stormer viscosity of about 60 to about 150 KU.

37. The set of prepaints of claim 32, wherein the extender prepaint further consists essentially of at least one additive selected from the group consisting of an acid, a base, a defoamer, a coalescent, a cosolvent, a mildewcide, a biocide and an antifreeze agent with the additive being present in an amount of less than about 20% by weight, based on the total weight of prepaint.

38. A paint line produced by a process which comprises the steps of:

- a. providing a set of different, but mutually compatible, fluid prepaints, which set comprises:

  - (i) at least one opacifying prepaint comprising at least one opacifying pigment,

- (ii) at least one extender prepaint comprising at least one extender pigment, and
- (iii) at least one binder prepaint comprising at least one latex polymeric binder; and

5 b. dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.

39. A set of different, but mutually compatible, fluid prepaints, sufficient to form at least one paint line useful as an elastomeric coating, which set comprises:

- (i) at least one opacifying prepaint comprising at least one opacifying pigment;
- (ii) at least one extender prepaint comprising at least one extender pigment; and
- (iii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of less than about 0° C.

40. A method of forming at least one paint line useful as an elastomeric coating, which method comprises the steps of:

- (a) providing a set of different, but mutually compatible, fluid prepaints, which set comprises:

  - (i) at least one opacifying prepaint comprising at least one opacifying pigment;
  - (ii) at least one extender prepaint comprising at least one extender pigment; and
  - (iii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of less than about 0° C.; and

- (b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.

41. A method of forming a range of paints, the range comprising at least two paint lines useful as an elastomeric coating, which method comprises the steps of:

- (a) providing a set of prepaints sufficient to formulate at least two paint lines, which set comprises:

  - (i) at least one opacifying prepaint comprising at least one opacifying pigment;
  - (ii) at least one extender prepaint comprising at least one extender pigment;
  - (iii) at least one binder prepaint comprising at least one latex polymeric binder having a Tg of less than about 0° C.; and
  - (iv) at least one additional different prepaint selected from the group consisting of (i), (ii), (iii), and (iv); and

- (b) dispensing a predetermined amount each of the prepaints into containers or applicators to form the range of paints.

42. A set of different, but mutually compatible, fluid prepaints sufficient to form at least one paint line useful as a non-cementitious, aggregate finish, which set comprises:

- (i) at least one opacifying prepaint comprising at least one opacifying pigment;
- (ii) at least one extender prepaint comprising at least one extender pigment;
- (iii) at least one binder prepaint comprising at least one latex polymeric binder; and
- (iv) at least one prepaint comprising an aggregate.

43. A method of forming at least one paint line useful as a non-cementitious, aggregate finish, which method comprises the steps of:

- (a) providing a set of different, but mutually compatible, fluid non-cementitious prepaints, which set comprises:

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- (i) at least one opacifying prepaint comprising at least one opacifying pigment;
- (ii) at least one extender prepaint comprising at least one extender pigment;
- (iii) at least one binder prepaint comprising at least one latex polymeric binder; and
- (iv) at least one prepaint comprising an aggregate; and

(b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.

44. A method of forming a range of paints, the range comprising at least two paint lines useful as a non-cementitious, aggregate finishing coating, which method comprises the steps of:

- (a) providing a set of different fluid, but mutually compatible, non-cementitious prepaints sufficient to formulate at least two paint lines, which set comprises
  - (i) at least one opacifying prepaint comprising at least one opacifying pigment;
  - (ii) at least one extender prepaint comprising at least one extender pigment;
  - (iii) at least one binder prepaint comprising at least one latex polymeric binder;
  - (iv) at least one prepaint comprising an aggregate; and
  - (v) at least one additional different, prepaint selected from the group consisting of (i), (ii), (iii), and (iv); and
- (b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the range of paints.

45. A set of different, but mutually compatible, fluid prepaints sufficient to formulate at least one paint line useful for forming pigmented and clear coatings, which set comprises:

- (i) at least one prepaint comprising at least one opacifying pigment; and

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- (ii) at least two prepaints each of which comprises at least one latex polymeric binder.

46. A set of different, but mutually compatible, fluid prepaints sufficient to form at least one paint line useful in graphics art applications, which set comprises:

- (i) at least one prepaint comprising at least one latex polymeric binder having a Tg of about -50° C. to about 10° C.;
- (ii) at least one prepaint comprising at least one latex polymeric binder having a Tg of about 50 to about 140° C.; and
- (iii) optionally, at least one prepaint comprising at least one latex polymeric binder having a Tg of about 0° C. to about 65° C.

47. The set of prepaints of claim 46, which further comprises at least one additional prepaint selected from the group consisting of a prepaint comprising at least one alkali-soluble resin, a prepaint comprising at least one gloss additive, a prepaint comprising at least one wax, and at least one prepaint comprising at least one pigment dispersion.

48. A method of forming at least one paint line, which method comprises the steps of:

- (a) providing the set of prepaints of claim 45, 46 or 47; and
- (b) dispensing a predetermined amount of each of the prepaints into containers or applicators to form the paint line.

49. The set of prepaints of claim 1 wherein the extender prepaint has a PVC of about 35% to about 100%.

50. The method of forming at least one paint line of claim 5 wherein the extender prepaint has a PVC of about 35% to about 100%.

\* \* \* \* \*

EXHIBIT  
B



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# United States Patent [19]

Brock et al.

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[45] Date of Patent: Sep. 30, 1997

[54] PROCESS FOR PREPARING AQUEOUS COATING AGENTS USING MODULAR SYSTEMS

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## Related U.S. Application Data

[63] Continuation of Ser. No. 184,587, Jan. 21, 1994, abandoned.

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[58] Field of Search 524/457, 507

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## ABSTRACT

A process for preparing aqueous coating agents with adjustable optical effects by mixing at least two storage-stable pre-mixed aqueous modules (units) is described, in which

- A) at least one aqueous special effect module containing one or more special effect pigments, one or more anionic and/or non-ionic stabilised water-dilutable binders, one or more organic solvents, at least 20 wt. % of water and optionally conventional lacquer additives, and
- B) at least one aqueous binder module containing one or more anionic and/or non-ionic stabilised water-dilutable binders, water, and optionally one or more organic solvents, one or more cross-linking agents and/or conventional lacquer additives, are mixed together.

18 Claims, No Drawings

PROCESS FOR PREPARING AQUEOUS  
COATING AGENTS USING MODULAR  
SYSTEMS

This is a continuation of application Ser. No. 08/184,587, filed Jan. 21, 1994 now abandoned.

The invention relates to a process for preparing aqueous coating agents with adjustable optical effects using modular systems (mixing systems). It is suitable in particular for preparing long-term storage-stable aqueous special effect base lacquers which may be used in particular for lacquering motor vehicles and motor vehicle parts.

The use of water-dilutable lacquer systems is steadily gaining acceptance in the motor vehicle and motor vehicle parts sector. There is a demand, especially in the area of aqueous special effect base lacquers, for a constantly increasing number of special effect shades, which renders efficient production and storage increasingly difficult. One way to solve this problem is the provision of a limited number of storable individual units, which are combined, depending on the desired special effect shade, to give the final, aqueous special effect base lacquer shortly before application.

Thus, EP-A-399 427 describes a water base lacquer modular system consisting of 5 units which, after combination, produce a final water base lacquer. In this case it is essential, according to the invention, that the special effect unit, the component with metal-containing pigments, must be prepared and stored in the absence of water. This is achieved by slurring metal-containing pigments in an alkyd, acrylate or polyester resin dissolved in a solvent and an organic solvent. Special effect units prepared in this way do not contain a neutralising agent for acid resins. The water base lacquers formulated therewith thus have an undesired high proportion of solvent and a separate neutralising unit is required. In addition, production of this water base lacquer requires strict observation of the mixing sequence for the individual units.

Furthermore, aqueous lacquers based on different units are described in EP-A-0 468 293 and EP-A-0 471 972. However, it is essential that the special effect unit contains no water.

DE-A-41 10 520 describes a mixing system which is intended to be suitable for preparing aqueous pigmented coating agents with precisely determined shades. It is intended in particular for preparing water base lacquers. The mixing system consists of various basic dyes (A), which contain less than 5 wt. % of water, preferably no water, and pigments, solvents and water-dilutable binders, and a pigment-free aqueous component (B) which contains in particular water-dilutable binders and/or rheological additives. The water-dilutable binders contained in component A are present in solvent form and must be capable of being prepared in solvent form. The water base lacquers formulated in this way therefore have undesired high proportions of solvent. The final coating agents are prepared by mixing the components just before application, they are not storage-stable.

The object of the invention is the provision of a process for preparing aqueous coating agents, in particular for preparing aqueous single-component special effect base lacquers with low solvent contents using a modular system or mixing system or unit system which is stable over a long period of time, wherein the individual modules in the system can easily be mixed with each other in order to produce a desired special effect.

It has been shown that this object can be achieved by the use of a modular system which contains a special effect module with a high water content.

The invention thus provides a process for preparing aqueous coating agents with adjustable optical effects by mixing at least two storage-stable pre-mixed aqueous modules, which is characterised in that

A) at least one aqueous special effect module containing one or more special effect pigments, one or more water-dilutable anionic and/or non-ionic stabilised binders, one or more organic solvents, at least 20 wt. % of water and optionally conventional lacquer additives and

B) at least one aqueous binder module containing one or more water-dilutable anionic and/or non-ionic stabilised binders, water, optionally one or more organic solvents, and optionally one or more cross-linking agents and/or one or more conventional lacquer additives, are mixed together.

The modular system used according to the invention may contain, in addition to special effect module A) and binder module B), for example,

C) at least one dye module containing one or more pigments and/or fillers, one or more anionic and/or non-ionic stabilised, water-dilutable binder and water, and optionally one or more organic solvents and/or conventional lacquer additives, and/or

D) at least one rheology module containing one or more organic or inorganic agents for regulating the rheology (rheology components) and water, and optionally one or more water-dilutable anionic and/or non-ionic stabilised binders and/or one or more organic solvents, and/or

E) at least one cross-linking module containing one or more cross-linking agents and optionally one or more organic solvents, water, one or more anionic and/or non-ionic stabilised water-dilutable binders and/or one or more conventional lacquer additives.

Here, modules are understood to be storage-stable units (mixing units) which can be stored separately, from which a final coating agent can be prepared by mixing, which optionally can still be adjusted to the application viscosity. By means of mixing the individual modules, desired adjustable special effects, and optionally adjustable shades of colour, can be obtained. The modules could be provided by the manufacturer in the form of a set containing, for example, at least modules A) and B).

Different embodiments may be prepared from each of the modules A) to E). A set of modules is produced in this way which may consist of one or more modules.

Special effect module A) is an aqueous preparation which contains at least one special effect pigment, at least one water-dilutable resin (binder) and at least 20 wt. % of water, a proportion of organic solvents and optionally conventional lacquer additives.

Special effect pigments are those pigments which produce a decorative effect in lacquer coatings and also, but not exclusively, may produce a coloured effect. Special effect pigments are distinguished in particular by a plate-like structure. Examples of special effect pigments are: metallic pigments, e.g. made from aluminium, steel, copper or other metals; interference pigments such as e.g. metal oxide coated metallic pigments, e.g. titanium dioxide coated or mixed oxide coated aluminium, coated micas such as e.g. titanium dioxide coated mica and graphite effect pigments.

A number of these special effect pigments is available commercially and they differ in particle size, particle size distribution and particle shape. The choice of pigment depends on the particular special effect desired in the lacquer

film. Special effect modules with only one pigment are preferably prepared. However, it is also possible to prepare special effect modules which contain several different special effect pigments.

Surprisingly, it has been shown, within the scope of the invention, that aqueous modules containing special effect pigments, especially metallic pigments, may be provided for the process according to the invention, wherein the metallic pigments may even consist of water-sensitive metals such as aluminium or steel. It has been shown that this is possible in particular when the special effect module contains 3 to 13 wt. %, especially 3.5 to 4 wt. % of the water-sensitive metallic pigment. The pH is then preferably 7.2 to 8.0, particularly preferably 7.5 to 8.0. The pigment/binder ratio in this case is preferably 0.02:1 to 10:1, with reference to the weight of solids. Due to the provision of this type of aqueous special effect module based on metallic pigments, a lacquer material which has a particularly low solvent content can be provided by the process according to the invention.

The water-dilutable resins contained in the special effect module may carry an anionic charge. Anionic resins in the form of aqueous solutions or dispersions neutralised with bases are available.

The water-dilutable resins contained in the special effect module may also be non-ionically stabilised. For example, those resins which are described later for binder module B) may be used.

In the case of anionic resins, the anionic groups are preferably present as neutralised carboxyl groups, corresponding to an acid value of preferably 15-70 mg KOH/g. Aqueous special effect modules containing anionic resins preferably have a pH of 7.0-9.0.

The resins may be conventional film-forming binders and/or paste resins. They may be based, for example, on polyesters, polyacrylates or polyurethanes, as explained in the description of the set of binder modules. Preferably, polyurethane resins are used as water-dilutable resins in the special effect module.

Water-dilutable or non-water-dilutable cross-linking components may also be contained in the special effect module. These cross-linking components are described in more detail in the description of the cross-linking module.

Preferably, each of the aqueous special effect pigment modules contains the same binder or binder mixture. This means that a constant binder composition can be produced, even when mixing different modules.

Furthermore, the special effect module may contain a small proportion of at least one water-miscible solvent, such as alcohols, e.g. monoalcohols such as butanol, n-propanol or isopropanol; ether alcohols, e.g. butoxyethanol, butoxypropanol or methoxypropanol; dialcohols such as glycols, e.g. ethylene glycol, polyethylene glycol; trialcohols such as glycerol; ketones, e.g. acetone, methylethyl ketone or N-methylpyrrolidone; ethers, e.g. dipropylene glycol dimethyl ether.

The special effect module preferably contains a rheology regulating agent. These may be the substances or mixtures which are described for the preparation of a rheology module. These may be directly added during preparation of the special effect module or admixed later as a finished rheology module.

Furthermore, conventional lacquer additives such as e.g. wetting agents, defoamers, neutralising agents and catalysts may be contained in the aqueous special effect module.

The aqueous special effect module is generally prepared in such a way that the special effect pigment, e.g. in the form of a commercially available paste, is initially introduced,

water-dilutable solvent and additives are added and then the aqueous resin solution is admixed under a shear force. Powdery special effect pigments are first processed with solvent and additives to produce a paste. Care should be taken that platelet-shaped special effect pigments are not mechanically damaged during the mixing process.

Aqueous storage-stable special effect modules with a preferred pigment/binder ratio of 0.02:1 to 10:1 are produced. The solids content of the whole special effect module is then preferably 10 to 40 wt. %. The ratio by weight of water to organic solvent in the aqueous special effect module is preferably 12:1 to 3:1. The water content of the special effect module is at least 20, preferably 20 to 75 wt. %.

Binder B) is an aqueous solution or dispersion of at least one anionic and/or non-ionic stabilised water-dilutable binder. These are film-forming resins or paste resins such as are normally used in aqueous coating agents, especially in aqueous base lacquers. They may be present alone or in combination. The film-forming resins may be based on polyesters, polyacrylates or preferably polyurethanes. They may be self-cross-linked or require an external cross-linking agent or dry out physically.

Examples of suitable non-ionically stabilised binders are those binders whose water-dilutability is achieved by the incorporation of polyether segments into the resin molecule. Examples of this type of stabilised polyurethane or polyurethanacrylate resin are described in EP-A-354 261, EP-A-422 357 and EP-A-424 705.

The aqueous binder module preferably contains anionic stabilised binders. Examples of these are (meth)acrylic copolymers, polyester resins or preferably polyurethane resins.

Examples of suitable water-dilutable (meth)acrylic copolymers can be found in EP-A-399 427 and EP-A-287 144.

Examples of suitable water-dilutable polyester resins are described in DE-A-29 26 584, DE-A-38 32 142 and EP-A-301 300.

It is also possible to use mixtures of such binders. Particularly suitable binders are those in which (meth)acrylic copolymers and polycondensation resin are present bonded covalently or in the form of interpenetrating resin molecules. Examples of these resins as this type of combination of (meth)acrylic copolymers and polyester resin are described in EP-A-226 171.

Examples of the particularly preferred anionic stabilised polyurethane resins are described in great variety in the literature. These are aqueous polyurethane dispersions or solutions or those binders in which (meth)acrylic copolymers and polyurethane resin are present bonded covalently or in the form of interpenetrating resin molecules. Suitable PU dispersions are stable, aqueous dispersions with a solids content of 20 to 50%. The molecular weight ( $M_w$ ) of the resins may vary over wide limits, from 1000 to 500000, wherein the molecular weights of film-forming binders lie in the upper range of numbers and those of paste resins lie in the lower range of numbers.

Examples of polyurethane dispersions which may be prepared by chain-lengthening prepolymers which contain isocyanate functions using polyamines and/or polyols, are found in EP-A-89 497, EP-A-228 003, DE-A-36 28 124 and EP-A-512 524.

Polyurethane dispersions which may be prepared by chain-lengthening prepolymers which contain isocyanate functions using water are described in DE-A-39 15 459.

Particularly preferred polyurethane dispersions of this type are described in P 42 24 617, from the same applicant,

which has not yet been laid open for public inspection. These are self-emulsifying polyurethane dispersions which preferably have an acid value, with reference to the solids content, in the non-neutralised state, of 5 to 50, particularly preferably of more than 10 and less than 30. The self-emulsifying urethane resin preferably has a glass transition temperature which is lower than the dispersing temperature. The dispersion may be prepared in such a way that, e.g. a urethane prepolymer is prepared by reacting

one or more polyisocyanates (a), preferably diisocyanates, with a polyetherdiol or polyesterdiol (b1) or a mixture thereof, and

optionally one or more low-molecular weight polyhydroxyl compounds (b2) and

one or more dimethylolalkanoic acids (c) in a NCO/OH ratio by equivalents of 1.1-2.0:1, preferably 1.1-1.9:1,

in a single or multi-stage reaction in a hydrophilic organic solvent which contains no active hydrogens. Subsequently chain-lengthening with water takes place, for example in the organic phase, wherein for example 0.5 to 3 moles of water are used per NCO group. The polymers thus obtained may be emulsified in further water after or during neutralisation with an amine and the organic solvent may be distilled off, if necessary.

Examples of polyurethane dispersions which are prepared by chain-lengthening of PU prepolymers which contain active hydrogens which react with polyisocyanates, using polyisocyanates, may be found in DE-A-39 03 804 and DE-A-40 01 841.

Further anionic stabilised polyurethane (PU) dispersions are described in P 42 28 510, from the same applicant, which has not yet been laid open to public inspection. These are aqueous polyurethane resin dispersions which are obtainable

by chain-lengthening of

one or more polyurethane resins which contain at least one CH-acid group in the molecule by reaction in aqueous or non-aqueous medium with

at least one compound which can react with at least two CH-acid groups and

optional transfer-of-a-reaction-product-obtained-in-non-aqueous-medium to the aqueous phase.

The dispersions are preferably prepared solvent-free. The binder preferably still contains reactive functional groups.

The polyurethane resin which contains at least one CH-acid group may be prepared by a variety of methods. This type of CH-acid PU resin is described, for example, in EP-A-0 367 051.

Another method for preparing a dispersion of this type of polyurethane resin is to react a polyurethane resin with at least one ionic group which contains OH groups, which may contain urea groupings, in an anhydrous medium, with at least one compound which has at least one functional group which is suitable for reaction with at least some of the OH groups in the polyurethane resin and in addition contains a CH-acid group and transferring the product obtained to the aqueous phase after neutralisation.

The chains in the dispersions are lengthened before or after transfer to the aqueous phase using a compound which can react with two CH-acid functions. Preferably, however, chain-lengthening is performed in aqueous dispersion.

Compounds suitable for chain-lengthening are those which can react with CH-acid centres. At least a two-fold possibility of reaction must be provided. Examples of such compounds are aldehydes or di- or polyisocyanates. Appropriate chain-lengthening reagents may be used separately or in combination.

Examples of anionic stabilised polyurethane-based binders which are suitable as a component of the aqueous binder

module in which (meth)acrylic copolymers and polyurethane resin, bonded covalently or in the form of interpenetrating resin molecules, are present are described, for example, in EP-A-353 797, EP-A-297 576, DE-A-41 22 265 and DE-A-41 22 266. These are polymer hybrids which are prepared by emulsion polymerisation of radically polymerisable monomers in the presence of anionic stabilised polyurethanes which optionally carry unsaturated functions.

These are preferably the type of polyurethane based binder described in DE-A-41 22 265.

These are polyurethane dispersions, prepared by radical-initiated polymerisation of polyurethane macromonomers with a proportion of carboxyl, phosphonic acid or sulphonic acid groups and lateral vinyl groups as well as optional terminal vinyl groups, hydroxyl, urethane, thiourethane and/or urea groups.

These polyurethane dispersions may, in principle, be prepared by a variety of methods. One method comprises, e.g. preparing a polyaddition product by polyaddition of polyhydroxy compounds from the group polyhydroxypolyethers, polyhydroxy-polyesters and polyhydroxypolycarbonates, also polyhydroxycarboxylic acids, dihydroxyporphonic acids or polyhydroxysulphonic acids as well as polyisocyanates and a monomer which contains at least two hydroxyl groups and at least one vinyl group. The proportions of reactants, in particular of polyisocyanate, are selected so that a macromonomer with terminal hydroxyl groups is produced. This macromonomer, which in addition contains carboxyl, phosphonic acid or sulphonic acid groups and lateral vinyl groups, is then neutralised, if the acid groups in the monomers which contained these groups were not used initially in the neutralised form.

To prepare the polyurethane dispersion, the macromonomers thus obtained, which contain vinyl groups, are converted into an aqueous dispersion by the addition of water and polymerised by radical-initiated polymerisation using methods which are known per se. During this polymerisation, if so-called reactive diluters are not present from the start, monomers are added which are then co-polymerised into the polyurethane.

These monomers are alpha,beta-unsaturated monomers. Examples of these are alpha,beta-unsaturated vinyl monomers such as alkylacrylates, -methacrylates and -crotonates with 1 to 20 carbon atoms in the alkyl chain, di-, tri- and tetraacrylates, -methacrylates and -crotonates of glycols, tri- and tetra-functional alcohols, substituted and unsubstituted acryl- and methacrylamides, vinyl ethers, alpha,beta-unsaturated aldehydes and ketones, vinylalkyl ketones with 1 to 20 carbon atoms in the alkyl chain, vinyl ethers, vinylesters, diesters of alpha,beta-unsaturated dicarboxylic acids, styrene, styrene derivatives, such as e.g. alpha-methylstyrene.

The polyurethane paste resins which are mentioned above, e.g. from DE-A-40 00 889, may also be used as anionic stabilised PU resins in the aqueous binder module B) according to the invention. These are urethanised oil-free polyesters which contain OH groups, prepared by reacting diisocyanates with an excess of a polyol mixture and lower molecular dialcohols, of which some also contain at least one acid group capable of forming an anion. The number average of the molecular mass of these PU binders is preferably 3000 to 200000, particularly preferably less than 50000.

The binder module B) needed to prepare aqueous base lacquers may consist of one aqueous binder. The aqueous binders may also, however, be present in combination. Thus, the binders are each prepared separately and stored as a

single module afterwards or they are prepared as a mixture of binders and then stored as a multi-component binder module.

The binder module B) preferably contains aqueous binders based on anionic stabilised polyurethanes. It may be expedient, if some, e.g. up to 50 wt. % of the PU binder, is replaced by resins based on a combination of (meth)acrylic copolymer and polyester resin.

Furthermore, binder module B) may contain water-dilutable binders based on cellulose.

Aqueous binder module B) may also contain amino resins and/or blocked polyisocyanates. The amino resins and blocked polyisocyanates may be water-dilutable or non-water-dilutable and are commented on under the description of the cross-linking module. They are present in a ratio of 40:60 to 5:95 with respect to the water-dilutable binder, each being with reference to the solid resin.

Rheology regulating agents may also be contained. Furthermore, the aqueous binder may contain small proportions of conventional solvents, preferably less than 5 wt. %. These may be the water-miscible solvents described for the special effect module. The solids content of the binder module is preferably 20 to 60 wt. %.

The binder module B) may contain neutralisation agents for the anionic resins. Bases are used for this. Examples are ammonia or organic amines such as triethylamine, N-methylmorpholine, aminoalcohols such as dimethyl-isopropanolamine, dimethylethanolamine, 2-amino-2-methylpropanol-1.

Aqueous binder module units which contain anionic resins have a pH of 7.0-8.5. The ratio of organic solvent to water in the aqueous binder module is up to 0.3:1, preferably less than 0.2:1.

The modular system (made from modules A) and B)) used according to the invention may also include at least one aqueous dye module C), which contains, in addition to at least one anionic and/or non-ionic stabilised water-dilutable binder, dye pigments and/or fillers and optionally additives. Each dye module C) preferably contains not more than 4 different dye pigments and/or fillers, particularly preferred aqueous dye modules being those which contain only one dye pigment or only one filler. Examples of inorganic or organic dye pigments or fillers which can be used in the dye module are titanium dioxide, micronised titanium dioxide, iron oxide pigments, carbon black, silicon dioxide, barium sulphate, micronised mica, talc, azo-dyes, phthalocyanin dyes, quinacridone or pyrrolopyrrole pigments.

The same water-dilutable anionic and/or non-ionic stabilised resins may be used as described for the binder module. These are preferably binders which carry an anionic charge which act as binder components in the final special effect base lacquer. The resins may be based on polyesters, acrylates or polyurethanes. The resins may be paste resins alone or in combination with film-forming binders or cross-linking agents. PU paste resins, as described in DE-A-40 00 889, are particularly preferred.

Each aqueous dye module C) preferably contains the same binder or mixture of binders. In addition, water-dilutable or non-water-dilutable cross-linking components may be contained in the dye module.

Furthermore, the dye module C) may contain small proportions of water-miscible solvents. Bases may also be contained as neutralisation agents. It may be convenient if dye module C) contains rheology regulating agents. Furthermore, conventional lacquer additives, such as e.g. wetting agents, defoamers and flow controllers, may be contained in aqueous dye module C).

The aqueous dye modules C) are generally prepared in such a way that the dye pigment or filler is ground into some of the aqueous binder or preferably into a paste resin. This takes place in equipment which is known to the person skilled in the art. Afterwards, the remaining amount of water-dilutable resin is added. This may be the same or a different binder from that used in the dispersing stage.

Aqueous, storage-stable dye modules C) are produced with a pigment/binder ratio of 0.01:1 to 10:1. The solids content is preferably 20 to 80 wt. %.

Dye modules which contain anionic resins have a pH of 7.0 to 10.0. The ratio of organic solvent to water in the aqueous dye modules is up to 0.3:1, preferably up to 0.2:1.

The modular system used according to the invention may contain a rheology module D). This contains water and one or more substances which regulate the flow behaviour of the final special effect base lacquer as a rheology component.

Examples of these are polymeric microparticles, such as are described, for example, in EP-A-38 127, inorganic sheet silicates, e.g. aluminium magnesium silicate, sodium magnesium sheet silicate and sodium magnesium fluorolithium sheet silicates of the montmorillonite type, associative thickeners, based on e.g. polyurethane or cellulose, polyvinylalcohols, synthetic polymers with ionic groups such as e.g. poly(meth)acrylic acid. These substances are commercially obtainable in a variety of forms.

The modular system used according to the invention may also contain a cross-linking module E). The cross-linking module E) is used in particular when the final aqueous special effect base lacquer being produced is being prepared with the use of resins which contain cross-linkable groups in the molecule.

Examples of cross-linking resins contained in the cross-linking module are amino resins and/or blocked isocyanates. These are partially or completely etherified amine/formaldehyde condensation resins and/or blocked polyisocyanates with at least two reactive sites per molecule.

Such amino resins are described, for example, in Ullmann's "Encyclopedia of Industrial Chemistry", 5th ed., vol. A2, chapter "Amino resins", pages 115-141 (1985) and Houben-Weyl, "Methoden der Organischen Chemie", vol. 14/2, pages 319-388 (1962). The resins are prepared according to the prior art and supplied by many firms as commercial products.

Examples of such amino resins are amine/formaldehyde condensation resins which are produced by the reaction of aldehydes with melamine, guanamine, benzoguanamine or dicyanodiamide. The alcohol groups in the aldehyde condensation products are then partially or completely etherified with alcohols.

Examples of blocked isocyanates are any di- and/or polyisocyanates in which the isocyanate groups have been reacted with a compound which contains active hydrogen. Appropriate prepolymers which contain isocyanate groups may also be used as di- and/or polyisocyanates. The organic di- and/or polyisocyanates have an average molecular weight of 112 to 2000 and expediently an average isocyanate functionality of 2 to 8. These are e.g. aliphatic, cycloaliphatic, aromatic, optionally also sterically hindered polyisocyanates. So-called "lacquer polyisocyanates" which are prepared from known diisocyanates are particularly suitable as polyisocyanates.

Typical examples of this type of polyisocyanate are propylene diisocyanate, tetramethylxylylene diisocyanate, trimethylene diisocyanate, hexamethylene diisocyanate, trimethylhexane diisocyanate, cyclohexene-1,3 and -1,4 diisocyanate, methylcyclohexane diisocyanate, 4,4'-

diphenylmethane diisocyanate, isophorone diisocyanate or dicyclohexylmethane diisocyanate.

Isocyanates which are convenient to use are polyisocyanates which also have urethane groups, which can be obtained by reacting excess amounts of diisocyanate with simple polyhydric alcohols with a molecular weight of 62 to 300, especially trimethylolpropane.

Lower molecular weight compounds for blocking NCO groups are known. Examples of these are aliphatic or cycloaliphatic alcohols, dialkylamino alcohols, oximes, lactams, imides, hydroxyalkyl esters, malonates or acetoacetates.

The cross-linking module may contain the cross-linking agent alone. However, it may also contain one or more organic solvents, water, one or more anionic and/or non-ionic stabilised, water-dilutable binders and/or one or more conventional lacquer additives. These are, for example, the same as those described for the other modules.

The different modules are storage-stable. They may be used in the modular system according to the invention. Furthermore, it is possible to mix several identical or different modules to give new storage-stable combination modules. For example, different special effect and/or dye modules may be mixed. Likewise, cross-linking modules and binder modules may be mixed. Likewise, the rheology module may be mixed with the special effect or the dye module. It has been shown to be expedient to select a modular system for mixing coating agents in which the special effect module and binder module and optionally the dye module are kept as separate entities. The rheology and/or cross-linking module may be present as separate entities or mixed with the other modular units.

The aqueous single component special effect base lacquer is prepared by simply mixing the special effect module with the binder module and optionally the dye module and/or the rheology module and/or the cross-linking module. Any sequence may be used for admixing, preferably, however, the module with the highest viscosity and the largest share of the volume is initially introduced. After mixing well, the application-viscosity is adjusted by the addition of deionised water.

The final special effect base lacquer prepared according to the invention has a solids content of preferably 10–40 wt. %, particularly preferably 15–30 wt. %, with a pigment/binder ratio of 0.06:1 to 0.6:1. The resin composition in the lacquer solids is preferably kept constant in each individual special effect base lacquer, wherein in the case of those special effect base lacquers which contain cross-linking agents there is a ratio of film-forming binder to cross-linking resins of 95:5 to 60:40 within the solid resin composition.

The proportion of solvent is less than 20 wt. %, preferably less than 10 wt. %. The pH of the aqueous base lacquer is the result of mixing the modular units. A correction to the pH is generally not required.

The final aqueous special effect base lacquer may be applied directly after mixing, but it may also be stored for longer than 12 months.

The aqueous special effect base lacquers prepared according to the invention may be applied using conventional methods. They are preferably applied by spraying in a dry layer thickness of 10–25 µm and processed using a wet-on-wet method, that is they are over-lacquered after an evaporation phase at 20°–80° C., using a conventional clear lacquer in a dry layer thickness of preferably 30–60 µm, and dried or cross-linked in common with this at temperatures between 20° and 140° C.

The multi-layered special effect lacquers obtained in this way correspond to the currently conventional requirements

for motor vehicle lacquers. The aqueous special effect base lacquers prepared according to the invention are thus suitable for lacquering vehicles and vehicle repairs, but they may also be used in other areas, such as e.g. lacquering plastics, in particular for lacquering motor vehicle parts.

The modular system used according to the invention consists of individual storage-stable modules. The modules contain film-forming binders which can be prepared in solvent form or in the aqueous phase. Low-solvent, aqueous, special effect base lacquers which have good long-term storage stability, can be prepared using the modular system used according to the invention. In particular, efficient storage and production of the aqueous special effect base lacquer is achieved.

15 The following examples explain the invention. All parts (P) refer to parts by weight.

#### EXAMPLE 1

Preparation of a PU dispersion in accordance with DE patent application P 42 24 617, which is not yet laid open to public inspection, preparation example 3:

20 1005 g of a linear polyester (formed from adipic acid, isophthalic acid and hexanediol with an OH value of 102) are heated to 90° C. in a reaction vessel with a stirrer, internal thermometer, heat-supply and reflux condenser and 1.8 g of trimethylolpropane and 393 g of isophorone diisocyanate are added at this temperature. The mix is held at this temperature until the NCO value is 3.8. After cooling to 60° C., a solution of 35.3 g of dimethylolpropionic acid, 26.1 g of triethylamine and 250 g of N-methylpyrrolidone are added. After heating to 80° C., the temperature is kept constant until an NCO value of 1.5 is reached. The molar amount of deionised water is admixed and the solution is held at 80° C. until isocyanate can no longer be detected. Finally, the mix is diluted with enough water to produce a liquid dispersion with a solids content of 34 wt. %.

#### EXAMPLE 2

40 Preparation of a special effect module A

The following components are contained in the special effect module:

45 32.0 parts of a conventional polyurethane dispersion (in accordance with DE-A-4122265, example 1) with 35 wt. % SC (SC=solids content),

13.4 parts of a commercially available aluminium paste containing 60 % aluminium, suitable for water base lacquers,

1.3 parts of an aluminium wetting additive based on organic phosphoric acid derivatives,

7.7 parts of n-butanol,

3.3 parts of a commercially available thickener based on polyacrylic acid,

3.3 parts of N,N-dimethylethanolamine.

The aluminium paste is initially introduced and mixed into a slurry with the solvent and additives. The binder is then added and mixed well.

#### EXAMPLE 3

Preparation of a special effect module B

35 parts of the PU dispersion from example 1, 20 parts of the aluminium paste from example 2, 2 parts of the wetting additive from example 2, 25 parts of butyl glycol, 1.8 parts of the thickener from example 2 and 0.2 parts of N,N-dimethylethanolamine are processed using the same method

as in example 2. Afterwards, the mixture is diluted with 16 parts of deionised Water.

## EXAMPLE 4

## Preparation of a binder module A

The following components are well mixed together with stirring:

42.0 parts of a conventional polyurethane dispersion (in accordance with DE-A-4122265, example 1) with 35% SC.

47.0 parts of completely demineralised water.

2.3 parts of n-butanol.

6.0 parts of butyl glycol.

1.4 parts of a commercially available thickener based on polyacrylic acid.

1.3 parts of N,N-dimethylethanolamine.

## EXAMPLE 5

## Preparation of a binder module B

26.2 parts of the PU dispersion from example 1, 8.8 parts of hexamethoxymethylmelamine, 5 parts of n-butanol, 3.5 parts of the thickener from example 2, 0.25 parts of N,N-dimethylethanolamine and 56.25 parts of deionised water were mixed together in the same way as in example 4.

## EXAMPLE 6

## Preparation of a blue dye module A

The dye module contains the following components:

42.0	parts of a conventional polyurethane paste resin (in accordance with DE-A-4000889) with 35% SC,
34.0	parts of a commercial blue copper phthalocyanine pigment,
5.0	parts of a dispersion aid (Disperse Ayd W22),
18.85	parts of completely demineralised water,
0.15	parts of N,N-dimethylethanolamine.

First, the pigment is made into a slurry in a mixture of additives and about half of the paste resin. Then the rest of the paste resin, amine and water are added and well mixed.

## EXAMPLE 7

## Preparation of a green dye module B

45 parts of the paste resin from example 6, 30 parts of a commercially available green phthalocyanine pigment, 5 parts of the dispersion aid from example 6, 2 parts of butyl glycol, 17.9 parts of deionised water and 0.1 parts of N,N-dimethylethanolamine are processed in the same way as in example 6.

## EXAMPLE 8

## Preparation of aqueous special effect base lacquers

Storage-stable special effect base lacquers are prepared by smoothly stirring together the modules cited in the Table:

SPECIAL EFFECT BASE LACQUERS

5	A (silver metallic)	B (silver metallic)	C (blue metallic)	D (green metallic)
Binder module A	70 P		60 p	
Binder module B		80 P		75 P
Sp. effect mod. A	30 P		20 P	
Sp. effect mod. B		20 P		15 P
10 Dye module A			20 P	
Dye module B				10 P

P = parts by weight

## We claim:

1. A process for preparing an adjustable optical effect aqueous coating agent comprising:

selecting at least one storage-stable, premixed, aqueous, special effect module A and at least one storage-stable, premixed, aqueous, binder module B, and

20 mixing at least modules A and B to form the coating agent, wherein

the aqueous special effect module A comprises at least one special effect pigment, at least one anionic or non-ionic stabilized water-dilutable polyurethane binder or a combination of at least one anionic binder and at least one non-ionic binder, at least one organic solvent and at least 20 wt-% of water, and

the binder module B comprises at least one anionic or non-ionic stabilized water-dilutable polyurethane binder or a combination of at least one anionic binder and at least one non-ionic binder and water.

2. A process according to claim 1 wherein the special effect pigment of special effect module A is metallic pigment or interference pigment or a combination thereof.

3. A process according to claim 1 wherein the binder of the special effect module A is at least one anionic stabilized water dilutable binder and the pH of the special effect module A is about 7 to about 9.

4. A process according to claim 1 wherein the special effect module A contains exclusively at least one metallic pigment as the special effect pigment, the metallic pigment content is from about 3 to about 13 wt % relative to the total weight of the components in module A, and the pigment to binder ratio of module A is from about 0.02:1 to about 10:1.

5. A process according to claim 1 wherein the special effect pigment of special effect module A is water-sensitive metallic pigment and module A has a pH of about 7.2 to 8.0.

6. A process according to claim 5 wherein the water sensitive metallic pigment is aluminum or steel or both.

7. A process according to claim 5 wherein the binder of special effect module A is at least one anionic stabilized binder.

8. A process according to claim 1 wherein special effect module A further comprises at least one conventional lacquer additive.

9. A process according to claim 1 wherein binder module B further comprises at least one organic solvent and at least one cross-linking agent.

10. A process according to claim 1 wherein more than one special effect module A is selected and each special effect module A contains the same binder or mixture of binders.

11. A process according to claim 1 wherein special effect module A has a water content of at least 50 wt % relative to the total weight of the module.

12. A process according to claim 1 wherein the binder of special effects module A or binder module B or both is at least one polyurethane resin.

13. A process according to claim 1 further comprising:  
 selecting at least one additional module from the group of  
 modules consisting of a dye module C, a rheology  
 module D, a cross-linking module E and any combi-  
 nation thereof; and,  
 mixing the selected additional module(s) with modules A  
 and B, wherein  
 the dye module C comprises at least one pigment or filler  
 or both, at least one anionic or non-ionic stabilized  
 water-dilutable binder or a combination of the anionic  
 binder and the non-ionic binder;  
 the rheology module D comprises at least one organic or  
 inorganic agent for regulating rheology, and water; and,  
 the cross-linking module E comprises at least one cross-  
 linking agent.

14. A process according to claim 13 wherein  
 the dye module C further comprises at least one organic  
 solvent,  
 the rheology module D further comprises at least an  
 anionic or non-ionic stabilized water-dilutable binder

or a combination of the anionic binder and the non-  
 ionic binder, and at least one organic solvent, and,  
 the cross-linking module E further comprises at least one  
 organic solvent, water and at least one anionic or  
 non-ionic stabilized water-dilutable binder or a combi-  
 nation of the anionic binder and the non-ionic binder.

15. A process according to claim 13 wherein dye module  
 C has a solids content of about 20 to about 80 wt. %.

16. A process according to claim 13 wherein the cross-  
 linking module E contains at least one blocked isocyanate or  
 at least one amine resin as the cross-linking agent.

17. A process according to claim 1 wherein the modules  
 are mixed in proportions such that a coating agent contain-  
 ing less than 20 wt. % of organic solvent is produced.

18. A process according to claim 13 wherein the modules  
 are mixed in proportions such that a coating agent contain-  
 ing less than 20 wt. % of organic solvent is produced.

\* \* \* \* \*

EXHIBIT  
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WELTORGANISATION FÜR GEISTIGES EIGENTUM  
Internationales Büro



INTERNATIONALE ANMELDUNG VERÖFFENTLICH NACH DEM VERTRAG ÜBER DIE  
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(54) Title: MODULAR SYSTEM AND PROCESS FOR PRODUCING AQUEOUS COATING COMPOSITIONS

(54) Bezeichnung: MODULSYSTEM UND VERFAHREN ZUR HERSTELLUNG WÄSSRIGER ÜBERZUGSMITTEL

(57) Abstract

A modular system is proposed for producing coating compositions, comprising: A) at least one aqueous binder module, containing cationically stabilized water-dilutable (meth)acryl copolymers and cationically stabilized water-dilutable polyurethane resins and/or cationically stabilized water-dilutable (meth)acrylated polyurethane resins, optionally in combination with non-ionically stabilized water-dilutable binders, water, and, optionally, organic solvents and/or additives usually used in paints, together with at least one of the following modules: B) one or more dye modules containing one or more water-containing dye pigments and/or fillers and cationically stabilized paste resins, at least 6 wt % water, as well as, optionally, water-dilutable cationically (and also optionally non-ionically) stabilized binders, organic solvents and/or additives usually used in paints, and/or C) one or more effect modules containing one or more water-containing effect pigments, at least 6 wt % water, cationically stabilized water-dilutable (meth)acrylated polyurethane resins which can optionally be present in combination with additional cationically or non-ionically stabilized water-dilutable binders, as well as optionally organic solvents and/or additives usually used in paints, and/or D) one or more cross-linking modules containing one or more cross-linking agents and optionally organic solvents, water and/or additives usually used in paints, and/or E) one or more rheological modules containing organic and/or inorganic agents for controlling rheological parameters, as well as optionally cationically or cationically and non-ionically and/or non-ionically stabilized water-dilutable binders and/or organic solvents and/or water.

(57) Zusammenfassung

Modulsystem zur Herstellung von wässrigen Überzugsmitteln, enthaltend A) mindestens ein wässriges kationisch stabilisierte wasserverdünnbare (Meth)acrylcopolymere und kationisch stabilisierte wasserverdünnbare Polyurethanharze und/oder kationisch stabilisierte wasserverdünnbare (meth)acrylierte Polyurethanharze, gegebenenfalls in Kombination mit nicht-ionisch stabilisierten wasserverdünnbaren Bindemitteln, Wasser sowie gegebenenfalls organische Lösemittel und/oder lackübliche Additive enthaltendes Bindemittelmodul, zusammen mit mindestens einem der folgenden Module: B) ein oder mehrere Wasser enthaltende Farbpigmente und/oder Füllstoffe und kationisch stabilisierte Pastenharze, mindestens 6 Gew.-% Wasser, sowie gegebenenfalls wasserverdünnbare kationisch und gegebenenfalls nicht-ionisch stabilisierte Bindemittel, organische Lösemittel und/oder lackübliche Additive enthaltende Farbmodule, und/oder C) ein oder mehrere Wasser enthaltende Effektpigmente, mindestens 6 Gew.-% Wasser, kationisch stabilisierte wasserverdünnbare (meth)acrylierte Polyurethanharze, die gegebenenfalls in Kombination mit weiteren kationisch oder nicht-ionisch stabilisierten wasserverdünnbaren Bindemitteln vorliegen können, sowie gegebenenfalls organische Lösemittel und/oder lackübliche Additive enthaltende Effektmodul und/oder D) ein oder mehrere Vernetzungsmittel sowie gegebenenfalls organische Lösemittel, Wasser und/oder lackübliche Additive enthaltende Vernetzermodule, und/oder E) ein oder mehrere organische und/oder anorganische die Rheologie steuernde Mittel sowie gegebenenfalls kationisch, oder kationisch und nicht-ionisch und/oder nicht-ionisch stabilisierte wasserverdünnbare Bindemittel und/oder organische Lösemittel und/oder Wasser enthaltende Rheologiemodule.



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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Modular System and Process for the Production of Aqueous Coating Compositions

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Modular system and process for the production of aqueous coating compositions.

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This invention relates to a modular system (a mixed system composed of modules), which is suitable for the production of various types of aqueous coating compositions. In particular, it is suitable both for the production of 10 aqueous effect base lacquers, single-tone aqueous base lacquers and aqueous single-coat topcoat lacquers with an adjustable colour tone and/or effect, and for the production of aqueous clear lacquers, which may in particular be used in automotive and automotive component 15 lacquer coating.

Water-borne lacquer systems are being used to an ever increasing extent in automotive and automotive component lacquer coating. Especially with regard to aqueous base 20 lacquers, there is, for example, a requirement for a constantly changing number of colour tones and effects, which is rendering economic production and storage increasingly difficult. One way to solve this problem is to provide a limited number of individual, storable components 25 which, depending upon the desired effect or colour tone, may be combined shortly before application to produce the finished, aqueous base lacquer.

EP-A-0 399 427 thus describes a modular aqueous base 30 lacquer system consisting of five components which, once combined, yield a complete aqueous base lacquer. In this process, the effect component, the component with the effect pigments, must be produced and stored without water. This is achieved by solubilising, for example, metal 35 pigments in a solvent-based solution of an alkyd, acrylate or polyester resin and in an organic solvent. The aqueous base lacquers formulated with this effect component thus have an undesirably high solvent content. Moreover, a separate neutralisation component is necessary which

contains ammonia to neutralise the acidic resins in the effect, resin and pigment component.

EP-A-0 468 293 and EP-A-0 471 972 also describe aqueous  
5 lacquers based on various components. It is, however, necessary for the effect component to be anhydrous. The resins contained in the effect component and pigment component are anionically or optionally non-ionically modified. In these cases too, a neutralising component  
10 containing ammonia is provided.

DE-A-4 110 520 describes a mixed system which is intended to be suitable for the production of aqueous pigmented coating compositions with precisely adjusted colour  
15 shading. In particular, aqueous base lacquers are to be produced using this method. The mixed system consists of various pigmented base coatings (A), which contain less than 5 wt.% of water, are preferably anhydrous and contain pigments, solvents and water-dilutable binders, and a  
20 pigment-free component (B) containing water, which in particular contains water-dilutable binders and/or rheological additives. The water-dilutable binders contained in component A) are present in organic solvents. The aqueous base lacquers formulated in this manner thus  
25 have an undesirably high solvent content. The complete coating compositions are produced by mixing the components directly before application, they are not stable in storage.  
30 The as yet unpublished German applications P 4 307 498 and P 4 301 991 from this applicant describe modular systems (mixed systems) for the production of aqueous single-tone and effect base lacquers, which each consist of a binder module and a colour and/or effect module. Both the binder  
35 module and the colour and effect module contain anionically and/or non-ionically stabilised water-dilutable resins.

The object of the present invention is to provide a modular system (mixed system) which, starting from a standard binder module, may be used for the production of various aqueous coating compositions, such as base lacquers, 5 single-coat topcoat lacquers and/or clear lacquers, by means of an appropriate combination of the individual modular components. In this system, both the individual modular components and the coating compositions which may be produced therefrom are intended to be stable in storage 10 for an extended period and to have a low solvent content. The individual modular components of the system are intended to be simply miscible with each other in order to produce the particular desired coating composition.

15 It has been found that this object may be achieved by the provision of an aqueous modular system on the basis of cationically stabilised resins. The modular system consists of at least two modular components, wherein one of the modular components is in each case a binder module and the 20 second modular component is selected from among a colour module, an effect module, a crosslinking module and/or a rheological module depending upon the use of the coating composition produced with the modular system or as a function of the desired achievable effect.

25

The present invention accordingly provides a modular system for the production of aqueous coating compositions, containing

30 A) at least one aqueous binder module containing one or more cationically stabilised water-dilutable (meth)acrylic copolymers and one or more cationically stabilised water-dilutable polyurethane resins and/or one or more cationically stabilised water-dilutable 35 (meth)acrylated polyurethane resins, optionally combined with non-ionically stabilised water-dilutable binders, water, optionally together with one or more

organic solvents and/or conventional lacquer additives,  
together with at least one of the following modules:

5 B) one or more colour modules containing water, one or more coloured pigments and/or extenders and one or more cationically stabilised polyurethane paste resins, at least 6 wt.% of water, optionally together with one or more water-dilutable cationically and optionally non-ionically stabilised binders, one or more organic solvents and/or conventional lacquer additives,  
and/or

10 15 C) one or more effect modules containing water, one or more effect pigments, at least 6 wt.% of water, one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may optionally be present combined with further cationically or non-ionically stabilised water-dilutable binders, optionally together with one or more organic solvents and/or conventional lacquer additives  
and/or

20 25 D) one or more crosslinking modules containing one or more crosslinking agents, optionally together with one or more organic solvents, water and/or conventional lacquer additives,  
and/or

30 35 E) one of more rheological modules containing one or more organic and/or inorganic rheological control agents, optionally together with one or more cationically, or cationically and non-ionically and/or non-ionically stabilised water-dilutable binders and/or one or more organic solvents and/or water.

Modules are here taken to be storage-stable components from which a complete coating composition may be produced by mixing, which composition may optionally still be adjusted to application viscosity.

5

It has been found that it is possible, by mixing the individual modules prepared according to the invention, to prepare various aqueous coating compositions, such as for example aqueous effect base lacquers, single-tone base lacquers, single-coat topcoat lacquers and clear lacquers, without needing to make use of different starting materials. This results in the advantage that coating compositions for different intended applications may be produced starting from standard components. This may be achieved by appropriate selection of the modular components defined within the modular system according to the invention; it is also possible to obtain desired adjustable colour tones and/or effects by mixing the individual modules.

20

It has been found that stable modules and complete systems may be obtained according to the invention if the colour and effect modules contain at least 6 wt.%, preferably at least 10 wt.%, of water.

25

Single-coat topcoat lacquers which may be produced from the modular system according to the invention should here be taken to be those coating compositions which form the final layer in multicoat lacquer coatings instead of the conventional two-coat base lacquer/clear lacquer structure.

Various embodiments of each of modules A) to E) may be prepared.

35 In addition to the stated modular system, the invention also relates to a process for the production of aqueous coating compositions by mixing at least one aqueous binder

component with further coating composition components, which process is characterised in that a supply of at least one storage-stable binder module A), together with at least one storage-stable colour module B), effect module C), 5 crosslinking module D) and/or rheological module E), is prepared and optionally stored, the modules being separately prepared, wherein the individual modules are mixed together as required in a quantities such that the 10 solids content arising therefrom, relative to the total solids content of the coating compositions, assumes the following percentages:

binder modules A): 5 - 99 wt.%  
colour modules B): 0 - 60 wt.%  
15 effect modules C): 0 - 50 wt.%  
crosslinking modules D): 0 - 50 wt.% and  
rheological modules E): 0 - 50 wt.%

wherein the sum of the percentages should amount to 100%.

20 In particular, aqueous coating compositions with a solids content of 10 to 80 wt.% at application viscosity are produced. The invention also relates to the aqueous coating compositions produced in accordance with the process 25 according to the invention.

According to a preferred embodiment, the binder module A) used according to the invention contains 10-99 wt.% of the cationically stabilised (meth)acrylic copolymer, 2-70 wt.% 30 of the cationically stabilised polyurethane resin and 0.2-60 wt.% of the cationically stabilised (meth)acrylated polyurethane resin, wherein the stated percentages relate to the total binder solids content in the binder module and should add up to 100%.

35 Cationically stabilised water-dilutable binders, optionally combined with non-ionically stabilised water-dilutable

binders are prepared in at least a proportion of the modules prepared according to the invention. "Cationically stabilised" should here and below also be taken to mean the term "cationically and additionally optionally 5 non-ionically stabilised". The term "water-dilutable" used here should also be taken to mean "water-soluble". The binders may in general be, for example, (meth)acrylic copolymers, polyurethane resins or (meth)acrylated polyurethane resins which have basic groups which form 10 cationic groups by at least partial neutralisation. The binders may be self or extrinsically crosslinking. These binders and the specific examples of these binders stated below are, as mentioned, generally usable in the modules 15 according to the invention; they are particularly conveniently suitable for binder module A).

Cationic (meth)acrylic copolymers, polyurethane resins and/or (meth)acrylated polyurethane resins may, for example, be those with a number average molecular weight 20 ( $M_n$ ) of 500 to 500000, an OH value of 0 to 450, an amine value of 20 to 200 and a glass transition temperature of -50°C to +150°C.

Examples of such cationic resins are described in 25 DE-A-41 34 301, DE-A-40 11 633, DE-A-41 34 290 and DE-A-42 03 510.

The (meth)acrylic copolymer resins containing basic groups preferably have an OH value of 30-200, a number average 30 molecular weight ( $M_n$ ) of 1000 to 200000 and an amine value of 15-150, particularly preferably an amine value of 25-100. On neutralisation, they are preferably present in aqueous systems at a pH value of 5 to 7. Particularly preferred (meth)acrylic copolymer resins have a number 35 average molecular weight ( $M_n$ ) of 4000 to 50000, a hydroxyl value of 60 to 175, an amine value of 20 to 100 and a glass transition temperature of -20 to +75°C. They may be

produced, for example, by solution polymerisation or emulsion polymerisation or copolymerisation using prior art methods, as for example described in DE-A-15 46 854, DE-A-23 25 177 or DE-A-23 57 152. They are produced, for 5 example, from (meth)acrylate monomers, optionally together with further free-radically polymerisable monomers. The free-radically polymerisable monomers, i.e. the (meth)acrylate monomers and/or further free-radically polymerisable monomers are at least in part monomers 10 containing amino groups or free-radically polymerisable monomers which may contain both amino groups and hydroxyl groups. They may be used mixed with other free-radically polymerisable monomers.

15 The method here is preferably to use 6 to 40 parts by weight of free-radically polymerisable monomers containing amino groups and 4 to 50 parts by weight of free-radically polymerisable monomers containing hydroxyl groups, or 8 to 60 parts by weight of free-radically polymerisable monomers 20 containing hydroxy and amino groups per 10 to 90 parts by weight of free-radically polymerisable monomers, which contain no further reactive groups. Of the free-radically polymerisable monomers used, preferably more than 50 wt.% and particularly preferably more than 70 wt.% are 25 (meth)acrylate monomers. These (meth)acrylate monomers may, by virtue of their ester functions, contain amino groups and/or hydroxyl groups or may occur as further non-functional monomers.

30 Suitable free-radically polymerisable monomers are virtually any ethylenically unsaturated monomers, as are common for free-radical polymerisation and which comply, for example, with Alfrey & Price's Q and e scheme for copolymerisation (c.f. Brandrup & Immergut, *Polymer* 35 *Handbuch*, 2nd edition, John Wiley & Sons, New York 1975). The basic poly(meth)acrylate resins may also contain onium groups, such as quaternary ammonium groups, sulphonium or

phosphonium groups, apart from or in addition to the amino groups.

Examples of free-radically polymerisable monomers containing hydroxyl groups are (meth)acrylic acid

5 hydroxyalkyl esters, such as for example 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 1,4-butanediol monoacrylate, 2,3-dihydroxypropyl methacrylate, pentaerythritol monomethacrylate, polypropylene glycol monoacrylate, adducts of (meth)acrylic acid and glycidyl esters, for example of versatic acid or also fumaric acid dihydroxyalkyl esters.

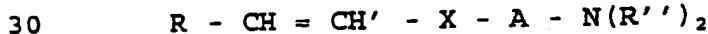
N-hydroxyalkyl (meth)acrylamide or N-hydroxyalkylfumaric acid mono- or diamides such as, for example,

N-hydroxymethyl-acrylamide or

15 N-(2-hydroxypropyl)methacrylamide may, however, also be used. Particularly elastic properties may be achieved by using a reaction product of hydroxyalkyl (meth)acrylates with  $\epsilon$ -caprolactone. Other compounds containing hydroxyl groups are allyl alcohol, monovinyl ethers of polyalcohols, 20 in particular of diols, such as for example the monovinyl ethers of ethylene glycol or butanediol, together with allyl ethers or esters containing hydroxyl groups, such as 2,3-dihydroxypropyl monoallyl ether, trimethylolpropane monoallyl ether or 2,3-dihydroxypropanoic acid allyl ether.

25 Hydroxyethyl, hydroxypropyl and/or 1,4-butanediol mono(meth)acrylate are particularly suitable.

Monomers containing amino groups which may be used are, for example, monomers of the general formula



wherein

R means -R' or -X-C<sub>n</sub>H<sub>2n+1</sub>,

R' means -H or -C<sub>n</sub>H<sub>2n+1</sub> and

R'' means -R', -C<sub>n</sub>H<sub>2n</sub>OH and/or -C<sub>n</sub>H<sub>2n</sub>NR<sub>2</sub>, wherein R is

35 defined as above, and

X means -COO-, -CONH-, -CH<sub>2</sub>O- or -O-,

A means  $-C_nH_{2n}-$  or  $-C_nH_{2n}-CHOH-CH_2$  and  
n means 1 to 8, preferably 1 to 3.

Examples of unsaturated monomers containing N groups are

5 N-dialkyl- or N-monoalkylaminoalkyl (meth)acrylate or the corresponding N-alkanol compounds, such as for example N-diethylaminoethyl acrylate or N-tert.-butylaminoethyl acrylate, N-dialkyl- or N-monoalkylaminoalkyl (meth)-acrylamide or the corresponding N-alkanol compounds, such

10 as for example N-dimethylaminoethanolacrylamide and/or heterocyclic compounds containing vinyl groups with one or more basic nitrogen atoms, such as for example N-vinylimidazole.

15 Component A) aminopoly(meth)acrylate resins may also, as described in DE 40 11 633, be produced by a polymer-analogous reaction. A copolymer containing acrylamide groups may thus, for example, be reacted with formaldehyde and a secondary amine and/or aminoalcohol. A particularly

20 preferred process is described in DE-A-34 36 346. In this process, monoethylenically unsaturated monomers containing epoxide groups are initially copolymerised to yield the copolymer. The product is then reacted with excess ammonia, primary and/or secondary monoamines and/or

25 monoaminoalcohols and the amine excess then removed by distillation.

A further suitable group of binders comprises, for example, cationically or cationically/non-ionically stabilised

30 polyurethanes. These may be synthesised from any conventional structural units known to the person skilled in the art. For example, during production of polyurethane resins, the equivalent ratio of the diisocyanate used is adjusted relative to the polyols and diols used in such a

35 manner that the complete polyurethane resin preferably has a number average molecular weight ( $M_n$ ) of 3000 to 200000, particularly preferably of 10000 to 40000 and an amine

value of 15 to 120, particularly preferably of 20 to 100. The pH value is preferably adjusted to 5 to 7 on neutralisation.

5 Urethanised polyesters, which may also be hydroxy-functional, constitute a preferred group of basic polyurethane resins, wherein, for example, basic groups in the form of amino groups are either directly condensed into the polyesters as aminoalcohols or, under milder  
10 conditions, are incorporated into the polymer chain by polyaddition or attached to the polymer chain. Thus, for example, a preferably linear polyester containing OH groups is synthesised by reacting the polyester with dialkyl-aminodialcohols and diisocyanates. If the reaction is  
15 performed with a substoichiometric quantity of isocyanate, the resin, once neutralised with acids, must be directly dispersible in water. If, on the other hand, an isocyanate excess is used, the resultant NCO prepolymer may be dispersed in water and converted into a polyurethane(urea)  
20 dispersion by chain extension with a polyamine. Such polyurethane(urea) dispersions may also be used according to the invention as polyurethane resins.

25 Polyurethane(urea) dispersions containing basic groups are produced in a known manner, for example by chain extension of a cationic prepolymer having a terminal isocyanate group with polyols, polyamines and/or hydrazine compounds, wherein chain extension is performed before or after neutralisation of the tert.-amino groups with these in  
30 water. The amine value is controlled by the quantity of compounds containing cationic groups in the prepolymer containing isocyanate groups used during production. Particle size is dependent upon the molecular weight of the polyol used, for example OH polyester (polyester polyol),  
35 the amine value and the sequence of synthesis. Number average molecular weight is preferably between 3000 and 500000, particularly preferably above 5000 and below 50000.

Polyurethane dispersions containing urea groups are preferably produced which contain at least 2, preferably 4 urethane groups and at least one tert.-amino group, especially a dialkylamine group in the NCO prepolymer.

5

A detailed description of the production of the polyurethane and polyurethane(urea) dispersions discussed above is given, for example, in DE-A-41 34 301 and DE-A-40 11 633.

10

Further binders which may readily be used in the binder module are those in which a cationic polyurethane resin and a (meth)acrylic copolymer are combined together in the form of interpenetrating resin molecules.

15

(Meth)acrylated polyurethane dispersions constitute a further group for the binder module A) which are also suitable for formulating effect modules. These are, for example, so-called polymer dispersions which are obtained 20 by emulsion polymerisation of (meth)acrylic monomers in polyurethane dispersions, which are cationically and/or non-ionically stabilised. The (meth)acrylic monomers used may also contain cationic groups, groups convertible into cationic groups (such as amino groups) and/or non-ionic 25 hydrophilic groups; such monomers may be used not only to stabilise already stabilised polyurethane dispersions, but also to stabilise polyurethanes which themselves do not yet contain any stabilising groups. Particularly preferred polyurethane dispersions are those which are copolymerised 30 by emulsion polymerisation of so-called polyurethane macromers, i.e. polyurethanes with covalently attached terminal and/or lateral vinyl groups, with unsaturated monomers, preferably (meth)acrylic acid derivatives. The amine value of such dispersions is from 5-150, preferably 35 from 10-100; the hydroxyl value from 0-150, preferably from 15-120.

According to a preferred embodiment, mixtures are used as the binder for the binder module A) which contain (meth)acrylic copolymers, as described above, and polyurethane resin. Suitable (meth)acrylate copolymers are 5 in particular those described above with an OH value of 30 to 200, a number average molecular weight ( $M_n$ ) of 100 to 200000 and an amine value of 15 to 150. Suitable polyurethane resins are in particular those described above with a number average molecular weight ( $M_n$ ) of 3000 to 10 200000 and an amine value of 15 to 120. These mixtures are also preferably present in the binder module at a pH value of 5 to 7.

In the cationically stabilised binders used according to 15 the invention, solubility may be influenced by the number of amino groups. The amine value should preferably be 20 to 200 mg KOH/g of solid resin, preferably between 30 and 150. Primary, secondary and/or tertiary amino groups may be present. Tertiary amino groups are preferred.

20 The hydroxyl value influences crosslinking density. It should preferably be between 20 and 400. Each binder molecule should here preferably contain an average of at least two reactive groups, for example OH or NH groups. 25 Reactivity is influenced by the nature of the groups, thus primary amino or hydroxyl groups are more reactive than secondary groups, wherein NH groups are more reactive than OH groups. It is preferred for the binder to contain reactive amino groups. The binders according to the 30 invention may bear further attached crosslinkable groups, for example blocked isocyanate groups, alkoxy silane groups or transesterifiable groups. In this case, these are self crosslinking binders. It is, however, possible additionally to mix crosslinking agents into the binders. The molecular 35 weight ( $M_n$ ) of the crosslinking agents is, for example, 500 to 20000, in particular 1000 to 10000. The crosslinking

agents may be present either directly in the binder module A) or in a separate crosslinking module (D).

The cationic binders may be physically drying, self or 5 extrinsically crosslinking; this applies in particular to the cationic binders contained in binder module A). The cationic binders may contain attached crosslinkable groups, for example blocked isocyanate groups or transesterifiable groups. In this case, these are self crosslinking binders. 10 It is, however, possible to add additional crosslinking agents in a separate crosslinking module.

The modules, in particular binder module A) may optionally also contain non-ionically stabilised binders.

15 Examples of suitable non-ionically stabilised binders are those binders in which water-dilutability is achieved by incorporating polyether segments into the resin molecule. Examples of such stabilised resins are polyurethane or 20 polyurethane acrylate resins, as are described in EP-A-0 354 261, EP-A-0 422 357 and EP-A-0 424 705.

The binder module A) necessarily contained in the modular system according to the invention may contain an aqueous 25 binder, but a combination of aqueous binders may also be present. The binders may here each be separately produced and then stored as individual modules or a mixture of the binders is produced and then stored as one or more multicomponent binder modules.

30 Binder module A) may contain rheological control agents and small proportions of conventional solvents, preferably less than 5 wt.%. The solids content of the binder module is preferably 10-50 wt.%, particularly preferably 15-40 wt.%.

35 Binder module A) contains neutralising agents for the basic resins. These are acids, preferably organic monocarboxylic

acids, such as for example formic acid, acetic acid, propionic acid. Hydroxycarboxylic acids are in particular well suited, such as for example lactic acid, glycolic acid, diglycolic acid, malic acid, citric acid, mandelic acid, tartaric acid, hydroxypropionic acid, dimethylolpropionic acid. The neutralising agents are added in the desired quantity to achieve water-compatibility or water-solubility. Neutralisation may be complete or partial. The pH value in binder module A) is preferably 5 to 7.

Colour module B) is an aqueous preparation which contains one or more coloured pigments and/or extenders, one or more cationically stabilised polyurethane paste resins, water 15 optionally together with water-dilutable cationic binders optionally combined with non-ionically stabilised binders, one or more organic solvents and/or conventional lacquer additives. Water is present in a quantity of at least 6 wt.%, preferably of at least 10 wt.%.

20 Each colour module B) preferably contains no more than four different coloured pigments and/or extenders, the aqueous colour modules particularly preferably contain only one coloured pigment or only one extender. The colour modules 25 of the systems according to the invention may contain conventional inorganic and/or organic coloured pigments and/or extenders as well as transparent pigments. Examples of inorganic or organic coloured pigments or extenders are titanium dioxide, micronised titanium dioxide, iron oxide 30 pigments, carbon black, silicon dioxide, barium sulphate, micronised mica, talcum, azo pigments, phthalocyanine pigments, quinacridone or pyrrolopyrrole pigments.

Cationically stabilised polyurethane paste resins which may 35 be used in the colour module preferably have a solids content (relative to the total weight of the colour module) of 20-50 wt.%, a viscosity of 0.5-50 mPa·s at 25°C and are

preferably 70 to 100% neutralised with monocarboxylic acids. Examples of suitable monocarboxylic acids are those already stated above in the description of the binder module.

5

Polyurethane paste resins preferably used in the colour module B) are, for example, basic polyesterurethane resins during the production of which the equivalent ratio of the diisocyanate used is adjusted relative to the polyols and 10 diols used in such a manner that the complete polyurethane resin, for example polyesterurethane resin, has a number average molecular weight ( $M_n$ ) of 3000 to 200000, preferably of below 50000. The OH value is preferably 0 to 80, particularly preferably 10 to 65; the amine value is 15 preferably 15 to 150, particularly preferably 10 to 100. The ratio of the OH groups of the polyol, for example polyester polyol and diol, to the NCO groups of the 20 isocyanates is preferably maintained above 1.0 to 1.2:1; the viscosity of the polyurethane resin, for example polyesterurethane resin, is preferably 1 to 30 Pa·s, particularly preferably above 2 and below 15 Pa·s, measured as a 60% solution in butoxyethanol at 25°C.

The colour module B) which may be used according to the 25 invention may, in addition to the basic polyurethane paste resin, contain cationically stabilised water-dilutable binders, optionally combined with non-ionically stabilised binders. These may, for example, be the same resins as have already been described in binder module A). Other 30 cationically stabilised binders may, however, also be included, for example polyester resins.

The colour module B) may furthermore contain small proportions of at least one water-miscible solvent, such as 35 alcohols, for example monoalcohols, such as butanol, n-propanol, isopropanol; ether alcohols, for example butoxyethanol, butoxypropanol, methoxypropanol, dialcohols,

such as glycols, for example ethylene glycol, polyethylene glycol; trialcohols such as glycerol; ketones, for example acetone, methyl ethyl ketone; N-methylpyrrolidone; ethers, for example dipropylene glycol dimethyl ether.

5

The module may, as already described in A), also contain acids as neutralising agents. Examples are organic monocarboxylic acids, such as for example formic acid, acetic acid, dimethylolpropionic acid.

10

It may be favourable for the colour module B) to contain one or more rheological control agents. These may, for example, be substances or mixtures as are described in the production of the rheological module E). These may be added 15 directly during production of the colour module or subsequently mixed in as a complete rheological module.

The colour module B) containing water may furthermore contain conventional lacquer additives; such as for example 20 wetting agents, defoaming agents, levelling agents, dispersion auxiliaries.

The colour module B) containing water is generally produced in such a manner that the coloured pigment and/or extender 25 is ground in the paste resin. The paste resin may be present in un-neutralised, partially neutralised or completely neutralised form in an organic, at least partially water-miscible solvent or in an aqueous solution or dispersion. Solutions or dispersions containing water 30 are preferred. This may proceed in conventional apparatus familiar to the person skilled in the art. The module is then optionally formulated with a further proportion of paste resin and/or the cationically and optionally non-ionically stabilised water-dilutable binders optionally 35 contained in the colour module (B) and/or further additives.

Storage-stable, aqueous colour modules (B) are obtained with a pigment or extender:binder ratio of, for example, 0.01:1 to 10:1, relative to solids weight. Solids content is preferably 20-80 wt.%.

5

The water content in the colour module is preferably at least 6 wt.%, particularly preferably at least 10 wt.%.

10 The effect module C) is an aqueous preparation which contains at least one or more effect pigments and water, optionally together with one or more organic solvents, one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may be present combined with non-ionically stabilised water-dilutable 15 binders, optionally together with one or more organic solvents and conventional lacquer additives.

Effect pigments are those pigments which bring about a decorative effect in lacquer coatings and additionally, but 20 not exclusively, may bring about a coloured effect. Effect pigments are in particular distinguished by a lamellar structure. Examples of effect pigments are: metal pigments, for example made of aluminium, copper or other metals; interference pigments, such as for example metal pigments 25 coated with metal oxides, for example aluminium coated with titanium dioxide or mixed oxide, coated micas, such as for example mica coated with titanium dioxide and graphite effect pigments.

30 Many such effect pigments varying in particle size and shape are commercially available. The pigments are selected on the basis of the desired effect in the lacquer film. Preferably, effect modules are produced with only one pigment. It is, however, possible for effect modules to 35 contain two or more different effect pigments.

The effect module may moreover contain small proportions of at least one water-miscible solvent, as for example described in A), such as alcohols, for example monoalcohols, such as butanol, n-propanol; ether alcohols, for example butoxyethanol, butoxypropanol, methoxypropanol; dialcohols, such as glycols, for example ethylene glycol, polyethylene glycol; trialcohols such as glycerol; ketones, for example acetone, methyl ethyl ketone, N-methyl-pyrrolidone; ethers, for example dipropylene glycol 10 dimethyl ether.

Examples of water-dilutable cationically stabilised (meth)acrylated polyurethanes usable in the effect module C) are those as were in particular described above for the 15 binder module A) as (meth)acrylated polyurethane dispersions, in particular with an amine value of 5 to 150, preferably of 10 to 100 and a hydroxyl value of 0 to 150, preferably of 15 to 120.

20 The effect module may contain rheological control agents. These may, for example, be substances or mixtures as are described below in the description of the rheological module E).

25 These may be added directly during production of the colour module or subsequently mixed in as a complete rheological module.

30 The aqueous effect module may furthermore contain conventional lacquer additives, such as for example wetting agents, defoaming agents, neutralising agents, catalysts.

35 The effect module containing water is generally produced in such a manner that the effect pigment, for example in the form of a conventional commercial paste, is initially introduced into a vessel, combined with water-dilutable

organic solvents and additives and optionally subsequently mixed with the aqueous resin solution with shearing.

Storage-stable, aqueous effect modules are obtained with a  
5 preferred pigment:binder weight ratio of 0.02:1 to 10:1. The solids content of the entire effect module is preferably 10-40 wt.%. The water content in the effect module is at least 6 wt.%, particularly preferably at least 10 wt.%.

10

The modular system according to the invention may also contain a crosslinking module D). The crosslinking module D) is in particular used in the event that the coating composition to be prepared is produced using those resins

15 which contain crosslinkable groups in their molecule.

Examples of crosslinking resins contained in the crosslinking module are conventional crosslinking agents, such as polyisocyanates, polyamines, blocked

polyisocyanates, amino resins, phenolic resins,

20 crosslinking agents containing siloxane groups and/or transesterification crosslinking agents.

The polyisocyanates may be any desired organic polyisocyanates with aliphatically, cycloaliphatically and/or aromatically attached free isocyanate groups. They are liquid at room temperature or liquefied by the addition of organic solvents. At 23°C, the polyisocyanates have a viscosity of, for example, 1 to 6000 mPa·s, preferably of above 5 and below 3000 mPa·s.

30

Such polyisocyanates are generally known and described, for example, in DE-A-38 29 587 or DE-A-42 26 243.

The polyisocyanates are preferably polyisocyanates or  
35 polyisocyanate mixtures with exclusively aliphatically and/or cycloaliphatically attached isocyanate groups with

an average NCO functionality of 1.5 to 5, preferably of 2 to 3.

Particularly suitable compounds are, for example, "lacquer polyisocyanates" based on hexamethylene diisocyanate, 5 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) and/or bis(isocyanatocyclohexyl)methane and the per se known derivatives of these diisocyanates with biuret, allophanate, urethane and/or isocyanurate groups, from 10 which the excess starting diisocyanate has been removed after production, preferably by distillation, down to a residual content of less than 0.5 wt. %.

Sterically hindered polyisocyanates of the general formula

15



20

are also very suitable, wherein

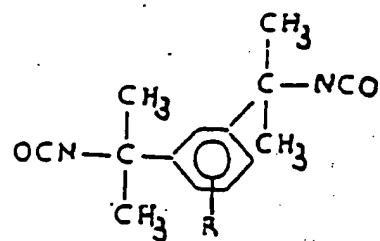
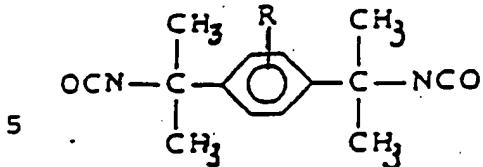
25  $\text{R}_1$  is H or  $\text{R}_2$ ,

$\text{R}_2$  is  $\text{C}_n\text{H}_{2n+1}$  with

n being 1 to 6.

Substituents  $\text{R}_1$  and  $\text{R}_2$  are either linear or branched, 30 identical or different. The parent structure A may consist of a single bond, an aromatic or alicyclic ring or an aliphatic linear or branched C chain with 1 to 12 C atoms.

Examples of such substances are 1,1,6,6-tetramethyl-35 hexamethylene diisocyanate, 1,5-dibutylpentamethyl diisocyanate, p- or m-tetramethylxylylene diisocyanate of the general formula



in which R means H or C<sub>1</sub>-C<sub>4</sub> alkyl, and the corresponding hydrogenated homologues, together with 2,3-bis-(8-isocyanatoethyl)-4-octyl-5-hexylcyclohexane and 3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate. These diisocyanates may also be reacted in a suitable manner to yield more highly functional compounds, for example by trimerisation or by reaction with water or trimethylolpropane.

Examples of blocked isocyanates are any desired di- and/or polyisocyanates in which the isocyanate groups are reacted with a compound containing active hydrogen. Corresponding prepolymers containing isocyanate groups may also be used as the di- and/or polyisocyanates. These are, for example, aliphatic, cycloaliphatic, aromatic, optionally also sterically hindered polyisocyanates, as have already been described above by way of example. Trifunctional, for example tri- to pentafunctional aromatic and/or aliphatic blocked isocyanates with a number average molecular weight of 500-1500 are preferred.

Conventional blocking agents may be used. Thus, for example, low molecular weight compounds containing acidic hydrogen are known for blocking NCO groups. Examples of such compounds are aliphatic or cycloaliphatic alcohols, dialkylaminoalcohols, oximes, lactams, heterocyclics containing NH groups, such as for example pyrazoles or triazoles, imides, hydroxyalkyl esters, esters of malonic acid or acetoacetic acid.

Amino resins are also suitable as crosslinking resins. Amino resins are described, for example, in Ullmann's *Encyclopedia of Industrial Chemistry*, 5th edition, volume A2, *Amino resins* entry, pages 115-141 (1985) and

5 Houben-Weyl, *Methoden der Organischen Chemie*, volume 14/2, pages 319-399 (1962). The resins are produced in accordance with the prior art and offered for sale by many companies as commercial products.

10 Examples of such amino resins are amine/formaldehyde condensation resins, which are produced by the reaction of aldehydes with melamine, guanamine, benzoguanamine or dicyanodiamide. The alcohol groups of the aldehyde condensation products are then partially or completely

15 etherified with alcohols.

Further examples of crosslinking agents which may also be contained in the crosslinking module are conventional transesterification crosslinking agents.

20 Transesterification crosslinking agents are polyesters containing no carboxyl groups with lateral or terminal  $\beta$ -hydroxyalkyl ester groups. These are esters of aromatic polycarboxylic acids, such as for example isophthalic acid, terephthalic acid, trimellitic acid or mixtures thereof.

25 These are condensed, for example, with ethylene glycol, neopentyl glycol, trimethylolpropane and/or pentaerythritol. The carboxyl groups are then reacted with optionally substituted 1,2-glycols to form  $\beta$ -hydroxyalkyl compounds. The 1,2-glycols may be substituted with

30 saturated or unsaturated alkyl, ether, ester or amide groups. The formation of hydroxyalkyl esters is also possible in which the carboxyl groups are reacted with substituted glycidyl groups, such as for example glycidyl ethers and glycidyl esters.

35 The transesterification crosslinking agents preferably contain more than 3  $\beta$ -hydroxyalkyl ester groups per

molecule and have a weight average molecular weight of 1000 to 10000, preferably of above 1500 and below 5000. The polyesters containing no carboxyl groups with lateral and terminal  $\beta$ -hydroxyalkyl ester groups may be produced as is 5 described, for example, in EP-A-0 012 463.

Polyamine crosslinking agents suitable as crosslinking resins are, for example, diamines and amines with more than two amino groups, wherein the amino groups may be primary 10 and/or secondary. Suitable polyamines are also adducts consisting of polyamines with at least two primary amino groups and which may be modified by further functional groups, for example with epoxy groups, with polyisocyanates or with (meth)acryloyl compounds. Polymers into which the 15 amino-functional groups are only subsequently introduced by reaction are also suitable as polyamines.

Examples of suitable polyamines are described in EP-A-0 240 083 or EP-A-0 346 982. Examples of these are 20 aliphatic and/or cycloaliphatic amines with 2-24 atoms, which contain 2-10 primary amino groups and 0-5 secondary amino groups. Examples of these are hexamethylenediamine, 1,2-diaminocyclohexane, isophoronediamine, diethylene-triamine or polyether polyamines.

25 Examples of conventional polyamines based upon modified polyfunctional amine components with di- or polyfunctional epoxy compounds are those produced using, for example, diglycidyl or polyglycidyl ethers based on bisphenol A or 30 bisphenol F, polyglycidyl ethers of phenolformaldehyde or novolaks; glycidyl ethers of fatty acids with 6-24 C atoms, epoxidised polybutadienes or resins containing glycidyl groups, such as polyesters or polyurethanes, which contain one or more glycidyl groups per molecule.

35 Polyamidoamines may also be used, as are, for example, described in EP-A-0 262 720. These are reaction products

prepared from mono- or polycarboxylic acids with polyamines which contain primary amino groups.

Polyamine/isocyanate adducts may also be used. Suitable 5 isocyanates for this purpose are the aliphatic, cycloaliphatic and/or aromatic di- or polyisocyanates conventional in the lacquer sector.

Further methods for the synthesis of amino-functionalised 10 curing agents are described in EP-A-0 002 801 and in EP-A-0 179 954. These are copolymers based on (meth)acrylic acid derivatives which are reacted and functionalised with diamines or alkyleneimines.

15 The crosslinking module D) may contain the crosslinking agent alone. It may, however, also contain one or more organic solvents, water and/or conventional lacquer additives. These are, for example, the same solvents and additives as are described for the other modules. The 20 module may in particular contain catalysts which accelerate the reaction between the binder and crosslinking component.

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When amine/formaldehyde resins are used, the catalysts used are, for example, amine salts or readily hydrolysable 25 esters of organic sulphonic acids or sulphonamides, as may be obtained as conventional commercial products. In the event of a combination with polyisocyanates, organometallic compounds, such as dibutyltin dilaurate may be used, optionally combined with basic catalysts, such as 30 1,4-diazabicyclo[2.2.2]octane.

The modular system according to the invention may also contain a rheological module E). This preferably contains water and, as the rheological component, one or more 35 substances controlling the flow properties of the finished aqueous effect base lacquer.

Examples thereof are polymer microparticles, as are for example described in EP-A-0 038 127, inorganic phyllosilicates, for example aluminium-magnesium silicate, sodium-magnesium phyllosilicates and sodium-magnesium-  
5 fluorolithium phyllosilicates of the montmorillonite type, associative thickeners, for example based on polyurethane or cellulose, polyvinyl alcohol, poly(meth)acrylamide, polyvinylpyrrolidone and polymeric urea compounds, synthetic polymers with ionic groups, such as for example 10 poly(meth)acrylic acid. These substances are commercially available in many forms.

Polyurethane-based cationic associative thickeners are preferred here.

15 The polyurethane-based associative thickeners are resins having the following schematic structure: hydrophilic segments such as polyether structures (wherein these 20 preferably contain a proportion of ethylene oxide units, preferably of 35% or more, in the event that only polyether structures are present) and/or cationic groups or groups convertible into cations are incorporated into the main polymer chain. In contrast, long-chain hydrophobic components are incorporated onto the chain ends. They are 25 responsible for the thickening action of such systems. They are synthesised in a similar manner to the polyurethane synthesis methods already described. Any usual starting materials for polyurethane synthesis available to the person skilled in the art are suitable for this purpose. 30 Long-chain fatty alcohols and fatty amines are preferably used as the hydrophobic modifiers. These contain, for example, a linear chain with at least 8, preferably at least 12 carbon atoms, wherein crosslinked fractions are also possible.

35 The amine value of associative thickeners is preferably 5 to 100, particularly preferably 10 to 90; the hydroxyl

value is 0 to 70, preferably 5 to 50. Naturally, in accordance with the conventional definition, the amine value and OH value in the present description each relate to mg of KOH per g of solid resin.

5

The various modules are stable in storage. Two or more identical or different modules may be mixed to yield novel storage-stable combined modules. Various effect and/or colour modules may, for example, be mixed together.

10

The invention provides an advantageous process for the production of various types of aqueous coating compositions based on a standard binder, which process is characterised in that a supply of each of the modules A) to E) according 15 to the invention is prepared and optionally stored, the modules being separately prepared, and, when required, the modules necessary for a particular application, such as for ~~example the quantities required to achieve a desired colour tone or effect, of the prepared modules A)~~ are mixed with 20 B) and/or C) and/or D) and/or E).

30

The aqueous coating compositions are produced by simply mixing the binder modules A) with the colour modules B), the effect modules C), the crosslinking modules D) and/or 25 the rheological modules E). Depending upon the selection of the second necessary modular component or the further possible modular components, various coating compositions may be produced, such as base lacquers, single-coat topcoat lacquers or clear lacquers.

30

Thus, for example, in order to produce clear lacquers, at least one binder module and at least one crosslinking module are mixed together. The binder modules used here are preferably based upon a binder combination of cationic 35 (meth)acrylic copolymer resins and cationic polyester-polyurethane resins. The preferred resins for this purpose are those described above for the binder module A).

Particularly preferred poly(meth)acrylate resins have a number average molecular weight ( $M_n$ ) of 4000-50000, a hydroxyl value of 60-175 mg KOH per g of solid resin and a glass transition temperature of -20 to +75°C. The amine 5 value is preferably 20-100 mg KOH per g of solid resin. The crosslinking module preferably contains those crosslinking agents based on blocked or unblocked polyisocyanates and/or melamine resins with at least two groups per molecule which are reactive towards amino and/or OH groups.

10

In order to produce clear lacquers, the modular system according to the invention preferably contains at least one rheological module. It is possible by means of a separate rheological module subsequently to influence rheology 15 during production of the coating composition. If the rheological agents are, for example, already contained in the binder module A), then the rheology of the complete ~~coating composition is predetermined by the binder. The rheological agents used here are preferably~~ polyurethane-based cationic associative thickeners, as have already been stated in the description of the rheological module.

The modular system may also contain transparent pigments, 25 for example transparent titanium dioxide, for the production of clear lacquers. The transparent pigments may be contained in a separate colorant module or in one of the other modules present.

30 A modular system according to the invention for the production of, in particular, effect base lacquers, preferably consists of a binder module A) based on a binder combination prepared from a cationic poly(meth)acrylate resin and a cationic polyurethane resin and an effect 35 module C) with a (meth)acrylated polyurethane dispersion as the binder and optionally a colour module B) with preferably one or more cationically stabilised polyester-

urethane resins as the binder together with a rheological module E) with preferably polyurethane-based cationic associative thickeners. The resins preferably used here are described in the binder module.

5

In order to produce, in particular, single-tone base lacquers and single-tone, single-coat topcoat lacquers, the modular system according to the invention may preferably contain at least one binder module A) based on a binder 10 combination prepared from a cationic poly(meth)acrylate resin and a cationic polyesterurethane resin, at least one colour module, wherein the colour module preferably contains the cationic polyurethane paste resins described above, and a rheological module based on polyurethane-based 15 cationic associative thickeners. A crosslinking module may be present in both the single-tone base lacquers and the single-tone, single-coat topcoat lacquers, which module contains, for example, melamine resin crosslinking agents and/or blocked polyisocyanates. Preferred resins are 20 described above in the binder and rheological modules.

The modules may be added in any desired sequence during production of the coating compositions. Preferably, however, the modules with the highest viscosities and the 25 highest proportions by volume are introduced initially. After mixing, application viscosity may be established by adding deionised water.

The coating compositions produced from the modular system 30 according to the invention preferably have a solvent content of below 20 wt.%, particularly preferably of below 10 wt.%.

The complete coating compositions may be applied directly 35 after mixing. They may, however, also be stored for longer than 12 months. In the case of room temperature

crosslinkable two-component coating compositions, the crosslinking module must, however, be separately stored.

5 A particular advantage of the modular system according to the invention is that the most varied coating compositions may be prepared in a simple manner from standard components. The present invention also provides these coating compositions.

10 The quantities listed below may, for example, here be used in the production of the coating compositions according to the invention. The quantities relate to the solids contents from the individual modules, which make up the total solids content of the coating composition (100 wt.%).

15 When producing aqueous effect base lacquers, the solids content from the binder module is preferably 10 to 99, particularly preferably 40 to 95 wt.%; the solids content from the colour module 0 to 40, preferably 0 to 30 wt.%; the solids content from the effect module preferably 0.01 to 50, particularly preferably 1 to 30 wt.%; the solids content from the crosslinking module 0 to 40, preferably 0 to 25 wt.% and the solids content from the rheological module preferably 0.01 to 50, particularly preferably 1 to 40 wt.%. In order to achieve application viscosity, the aqueous effect base lacquer is preferably adjusted to a total lacquer solids content of 10 to 55 wt.%, particularly preferably of 12 to 40 wt.%.

30 When producing single-tone aqueous base lacquers, the solids content from the binder module is preferably 5 to 60 wt.%, particularly preferably 8 to 50 wt.%; from the colour module preferably 1 to 60, particularly preferably 3 to 50 wt.%; from the crosslinking module 0 to 40, preferably 0 to 25 wt.% and from the rheological module 0 to 40, preferably 1 to 30 wt.%. The solids content of the single-tone aqueous base lacquer is adjusted to application

viscosity with a solids content of preferably 10 to 60 wt.%, particularly preferably of 12 to 45 wt.%.

In order to produce single-coat topcoat lacquers, the  
5 solids content from the binder module is preferably 5 to 60 wt.%, particularly preferably 8 to 50 wt.%; the solids content from the colour module preferably 0.5 to 60 wt.%, particularly preferably 1 to 45 wt.%; from the effect module 0 to 50 wt.%, preferably 0 to 30 wt.%; from the  
10 crosslinking module preferably 0.5 to 40 wt.%, particularly preferably 1 to 35 wt.% and from the rheological module 0 to 40 wt.%, preferably 1 to 30 wt.%. At application viscosity, the total solids content of the single-coat topcoat lacquer is preferably 10 to 70 wt.%, particularly  
15 preferably 12 to 50 wt.%.

When producing clear lacquers, the solids content from binder module is preferably 15 to 90 wt.%, particularly preferably 35 to 85 wt.%; from the colour module 0 to 20,  
20 preferably 0 to 10 wt.%; from the effect module 0 to 10, preferably 0 to 5 wt.%; from the crosslinking module preferably 0.01 to 50 wt.%, particularly preferably 2 to 40 wt.%; from the rheological module 0 to 40 wt.%, particularly preferably 1 to 30 wt.%. At application  
25 viscosity, the total lacquer solids content of the clear lacquer is preferably 10 to 80 wt.%, particularly preferably 12 to 65 wt.%.

The aqueous coating compositions produced from the modular  
30 system according to the invention may be applied using conventional methods, for example by spraying. Curing may proceed at, for example, between 20°C and 140°C.

A preferred option for application is to apply a base  
35 lacquer produced with the modular system according to the invention and, after a flashing-off stage at 20°C-80°C, to apply a conventional clear lacquer or a clear lacquer

produced with the modular system according to the invention using the wet-on-wet method and curing both layers together.

5 The multicoat lacquer coatings obtained in this manner satisfy today's conventional requirements for automotive lacquer coating. They are suitable for automotive original and repair lacquer coating, but they may also be used in other sectors, for example for lacquer coating plastics,  
10 wood or ceramics.

The modular system according to the invention consists of individual storage-stable modules which may simply and readily be mixed together. Low-solvent, aqueous coating compositions with good long term storage stability may be produced. Storage and production of the various coating compositions, such as base lacquers, topcoat lacquers and clear lacquers, are rationalised by means of a single modular system. A particular advantage of the system  
15 according to the invention and of the process according to the invention is that the most varied coating compositions may be prepared on the basis of standard modules.

20 The following examples are intended to illustrate the invention in greater detail.

#### Production examples for binder

##### Production example 1:

966 g of ethoxypropanol are heated under inert gas to 100°C  
30 with a reflux condenser being used. Within a period of 4 hours, a mixture of 195.5 g of hydroxyethyl methacrylate, 599 g of butanediol monoacrylate, 592 g of n-butyl methacrylate, 483 g of 2-ethylhexyl methacrylate, 439 g of butyl methacrylate, 439 g of methyl methacrylate, 893 g of  
35 styrene, 358 g of 3'-dimethylaminopropylmethacrylamide and 46 g of t.-butyl peroctoate is added. The temperature is then maintained at 110°C for 1 hour, 8.4 g of t.butyl

peroctoate dissolved in 12.2 g of ethoxypropanol are added and this operation is repeated one hour later. After 3 hours at 110°C, the following intermediate values are determined:

5

Solids content: 79.6 (30 minutes 150°C)  
Viscosity: 12.5 Pa·s (50% in ethoxypropanol at 25°C)

10 Production of the aqueous dispersion:

4 g of formic acid solution (50% in water) and 32.6 g of ethylene glycol monobutyl ether are thoroughly incorporated into 250 g of the aminoacrylate described above and 713.4 g 15 of completely deionised water are then added to produce the dispersion. After 2 hours' stirring, a finely divided aqueous aminoacrylate dispersion is obtained.

Characteristics:

20 Solids content: 20.4 wt.% (60 minutes 150°C)  
Acid mEq: 21 mEq/100 g of solid resin  
pH value: 6.5

Production example 2:

25 (Production example 1 in DE-A-4 011 633)

725 g of butoxyethanol are heated under inert gas to 110°C with a reflux condenser being used. Within a period of 3 hours, a mixture of 192 g of hydroxyethyl methacrylate, 30 137 g of butanediol monoacrylate, 288 g of glycidyl methacrylate, 364 g of 2-ethylhexyl acrylate, 439 g of butyl methacrylate, 439 g of methyl methacrylate, 90 g of styrene and 44 g of azobisisobutyronitrile are added. Then, after 1 hour at 110°C, a solids content of 72.2 wt.% is 35 measured and, after dilution to 60 wt.% with butoxyethanol, a viscosity of 2.14 Pa·s at 25°C is measured. After cooling to 50°C, a mixture of 120 g of diethylamine and 201 g of

isopropanol is added rapidly (1.10 mol of amine for 1.00 mol of epoxide). After 30 minutes, the temperature is raised to 65°C, maintained for 2 hours, then raised to 105 to 110°C and maintained for 3 hours. After cooling to 80°C,

5 isopropanol and excess amine are carefully removed by vacuum distillation. Solids content is adjusted to approximately 80 wt.% with butoxypropanol.

Intermediate value:

10

Solids content: 79.7% (30 minutes 150°C)

Amine value: 45 mg KOH per g of solid resin

Viscosity: 3.44 Pa·s (60% in butoxyethanol at 25°C)

15

Production example 3:

855 g of a polyester polyol (produced from neopentyl glycol, hexanediol and isophthalic acid with an OH value of 20 102 and an acid value 1) are mixed at approximately 45°C under inert gas with 138 g of methyldiethanolamine and 300 g of acetone in a reaction vessel with a stirrer, internal thermometer, heater and reflux condenser. 410.5 g of isophorone diisocyanate are then added and the 25 exothermic reaction is maintained at 80°C by cooling and heating until virtually no free isocyanate may any longer be detected (NCO value less than 0.2). At 40°C, 88.6 g of lactic acid in 200 g of water are added and thoroughly incorporated. 2902 g of completely deionised water are then 30 added to produce the dispersion. After 2 hours' stirring at room temperature, a finely divided polyurethane dispersion is obtained.

## Final values:

30 Solids content: 34.2 wt.% (60 minutes 150°C)  
Acid mEq: 66 mEq/100 of solid resin  
5 pH value: 5.6

## Production example 4:

912 g of a polyester (produced from adipic acid,  
10 isophthalic acid, 1,6-hexanediol and neopentyl glycol with  
an OH value of 113 and an acid value 1) are mixed at  
approximately 45°C under inert gas with 191 g of  
methyldiethanolamine and 185 g of N-methylpyrrolidone in a  
reaction vessel with a stirrer, internal thermometer,  
15 heater and reflux condenser. 697 g of isophorone  
diisocyanate are then added and the exothermic reaction is  
maintained at 80°C by cooling and heating until the NCO  
value is approximately 3.3. After the addition of 185 g of  
N-methylpyrrolidone, 184 g of hydroxyethyl methacrylate are  
20 added and the temperature maintained at 60°C until no free  
isocyanate may any longer be detected.

At 40°C, 74.1 g of formic acid in 152 g of water are added  
and thoroughly incorporated. 2026 g of completely deionised  
25 water are then added to produce the dispersion. After 2  
hours' stirring at room temperature, a finely divided  
polyurethane dispersion is obtained.

## Final values:

30 Solids content: 44.0 wt.% (60 minutes 150°C)  
Amine value: 45 mg KOH

## Production example 5:

35 30 g of the polyurethane dispersion from production example  
4 are diluted with 25 g of completely deionised water and

heated to 80°C. An emulsion prepared from 0.23 g of hexanediol diacrylate, 0.45 g of lauryl acrylate, 2.0 g of styrene, 1.2 g of ethylhexyl acrylate, 1.6 g of hydroxyethyl acrylate, 3.1 g of n-butyl methacrylate and 5 0.4 g of azoisobutyronitrile in 14 g of the polyurethane dispersion from production example 4 and 10 g of completely deionised water is added over a period of 3.5 hours at 80°C. This temperature is then maintained for one hour, then an emulsion of 0.1 g of azoisobutyronitrile in 2.3 g 10 of polyurethane dispersion from production example 4 is added and the temperature maintained at 80°C for one more hour. A finely divided dispersion with the following characteristics is obtained:

15 Solids content: 31.8 wt.% (1 hour 150°C)  
Amine value: 32 mg KOH/g  
pH value: 5.1

**Production example 6:**

20 909 g of a polycaprolactone diol with an OH value of 112 and an acid value of 1 is mixed under inert gas at approximately 45°C with 141.5 g of methyldiethanolamine in a reaction vessel with a stirrer, internal thermometer, 25 heater and reflux condenser. 442.5 g of isophorone diisocyanate are then added and the exothermic reaction is maintained at 80°C by cooling and heating until virtually no free isocyanate may any longer be detected (NCO value of less than 0.2).

30 96.5 g of lactic acid in 152 g of water are added at 60°C and thoroughly incorporated. 2759 g of completely deionised water are then added to produce the dispersion. After 2 hours' stirring at room temperature, a finely divided 35 polyurethane dispersion is obtained.

## Final values:

30 Solids content: 33.5 wt.% (60 minutes 150°C)  
Amine value: 45 mg KOH  
5 Acid mEq: 75 mEq/100 solid resin

## Production example 7:

10 682.5 g of a polyester diol (produced from neopentyl glycol, cyclohexanedicarboxylic acid and isophthalic acid with an OH value of 49 and an acid value of 1.3), 27 g of pentaerythritol, 148.3 g of dodecanol and 508 g of N-methylpyrrolidone are mixed under inert gas at approximately 45°C with 153 g of methyldiethanolamine in a 15 reaction vessel with a stirrer, internal thermometer, heater and reflux condenser. 529 g of isophorone diisocyanate are then added and the exothermic reaction is maintained at 80°C by cooling and heating until virtually no free isocyanate may any longer be detected (NCO value of 20 less than 0.2).

118 g of formic acid (50% in water) are added at 50°C and thoroughly incorporated. 2828 g of completely deionised water are then added to produce the dispersion. After 2 25 hours' stirring at room temperature, a finely divided polyurethane dispersion is obtained.

## Final values:

30 Solids content: 32.3 wt.% (60 minutes 150°C)  
Acid mEq: 84 mEq/100 g solid resin  
pH value: 5.2

## Production examples for the individual modules:

## Binder modules:

5 The binder modules are produced by thoroughly stirring together their constituents:

## Binder module I:

## 10 Constituents:

172.0 g	binder (according to production example 5)
28.5 g	binder according to production example 3
234.5 g	binder according to production example 1
15 30.0 g	completely deionised water

## Binder module II:

## Constituents:

20	
70.4 g	binder according to example 1
5.3 g	binder according to example 3
4.3 g	completely deionised water

## 25 Binder module III:

## Constituents:

30	47.3 g	binder according to example 2
	5.2 g	binder according to example 3
	3.2 g	completely deionised water

#### **Binder module IV:**

### Constituents:

5 31.3 g binder according to example 5  
 24.5 g binder according to example 2  
 2.5 g binder according to example 3  
 1.2 g ethylene glycol monobutyl ether  
 13.0 g completely deionised water

10

## Rheological module I:

100 g of the binder according to example 7 are mixed with 2 g of ethylene glycol monobutyl ether and 10 g of 15 completely deionised water.

### Effect modules:

For production of the effect modules, the particular effect 20 pigment is initially introduced into a vessel and solvents, wetting additives and binders are then thoroughly stirred in.

### Effect module I:

25

### Constituents:

30 8.4 g of a conventional commercial aluminium paste suitable for aqueous base lacquers with 65% aluminium

30 0.8 g of an aluminium wetting additive based on organic phosphoric acid derivatives

35 4.9 g ethylene glycol monobutyl ether

35 2.0 g N-methylpyrrolidone

35 4.5 g n-butanol

35 8.0 g binder according to production example 5

The module has a water content of 8.9 wt. %.

## Effect module II:

## Constituents:

5    12.8 g    of a conventional commercial iriodine pigment  
      2.7 g    of a conventional commercial wetting additive  
      2.7 g    n-butanol  
      1.1 g    N-methylpyrrolidone  
      8.0 g    binder according to production example 5

10

The effect module has a water content of 9.3 wt.%.

## Colour modules:

## 15 Blue colour module:

41.1 g    binder according to example 6  
1.1 g    of a conventional commercial dispersion auxiliary  
0.6 g    ethylene glycol monobutyl ether  
20    33.9 g    of a conventional commercial blue copper  
                  phthalocyanine pigment  
10.5 g    completely deionised water

## Red colour module:

25

## Constituents:

44.0 g    binder according to example 6  
1.6 g    of a conventional commercial dispersion auxiliary  
30    2.9 g    ethylene glycol monobutyl ether  
      34.5 g    of a conventional commercial red pigment  
      17.1 g    completely deionised water

## Black colour module:

## Constituents:

5      48.9 g    binder according to example 6  
      1.2 g    of a conventional commercial dispersion auxiliary  
      5.0 g    ethylene glycol monobutyl ether  
      13.5 g    of a conventional commercial carbon black pigment  
      15.6 g    completely deionised water

10

The pigment is ground in the stated mixture with an appropriate apparatus.

## Crosslinking module:

15

## Crosslinking module I (melamine resin mixture):

6.5 g    Cymel 373  
3.5 g    completely deionised water

20

## Crosslinking module II:

9.7 g    Luwipal 012  
2.0 g    of a conventional commercial isocyanate blocked  
25        with butanone oxime and based on isophorone  
          diisocyanate  
1.3 g    ethylene glycol monobutyl ether

## Crosslinking module III:

30

3.0 g    Cymel 327  
7.0 g    completely deionised water

## Crosslinking module IV:

35

8.1 g    Setamin US 138  
6.9 g    ethylene glycol monobutyl ether

**Production of aqueous base lacquers**

Storage-stable, aqueous effect lacquers are produced by uniformly mixing together the modules stated in the table.

5 They are adjusted to the desired application viscosity with water. The stated values are parts by weight.

**Effect base lacquers:**

		A Silver metallic	B Silver metallic	C Silver	D Blue metallic
10	<b>Binder module I</b>	68.9	71.2		
	<b>Binder module IV</b>			72.6	72.6
	<b>Effect module I</b>	15.0		15.0	15.0
	<b>Effect module II</b>		20.1		
15	<b>Rheological module I</b>	8.5	9.0	10.5	10.5
	<b>Crosslinking module I</b>			10	10
	<b>Blue-colour module</b>				4

20 Single-tone base lacquers & single-tone, single-coat topcoat lacquers:

		A Blue	B Black	C Red	D Red	E Topcoat lacquer
	<b>Binder module II</b>	80.6	76.5	76.2		75.5
25	<b>Binder module III</b>				55.7	
	<b>Rheological module I</b>	10.4	9.6	7.8	10.4	10.5
	<b>Crosslinking module III</b>				10	11
	<b>Blue colour module</b>	10.5				13.4
	<b>Red colour module</b>			12.45	15.9	
30	<b>Black colour module</b>		14.23			

Aqueous single-tone lacquers are obtained by mixing the above-stated components. They are adjusted to the particular desired application viscosity with water.

They may be used as aqueous base lacquers and single-tone, single-coat topcoat lacquers.

**Aqueous clear lacquer**

5

	A	B	C	D	E
Binder module II	76.2	76.5	76.2	76.5	76.5
Thickening module I	9.0	9.6	9.0	10.2	9.6
Crosslinking module I	10				6.5
10 Crosslinking module II		13.2			
Crosslinking module III			10.0		
Crosslinking module IV				15.0	10.5

Patent Claims:

5 1. Modular system for the production of aqueous coating compositions, containing

10 A) at least one aqueous binder module containing one or more cationically stabilised water-dilutable (meth)acrylic copolymers and one or more cationically stabilised water-dilutable polyurethane resins and/or one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, optionally combined with non-ionically stabilised water-dilutable binders, water, optionally together with one or more organic solvents and/or conventional lacquer additives, together with at least one of the following modules:

20 B) one or more colour modules containing water, one or more coloured pigments and/or extenders and one or more cationically stabilised polyurethane paste resins, at least 6 wt.% of water, optionally together with one or more water-dilutable cationically and optionally non-ionically stabilised binders, one or more organic solvents and/or conventional lacquer additives, and/or

25 C) one or more effect modules containing water, one or more effect pigments, at least 6 wt.% of water, one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may optionally be present combined with further cationically or non-ionically stabilised water-dilutable binders, optionally together with one or more organic solvents and/or conventional lacquer additives and/or

30

35

D) one or more crosslinking modules containing one or more crosslinking agents, optionally together with one or more organic solvents, water and/or conventional lacquer additives, and/or

5

E) one or more rheological modules containing one or more organic and/or inorganic rheological control agents, optionally together with one or more cationically, or cationically and non-ionically and/or non-ionically stabilised water-dilutable binders and/or one or more organic solvents and/or water.

10

2. Process for the production of aqueous coating compositions by mixing at least one aqueous binder component with further coating composition components, characterised in that a supply of at least one storage-stable binder module A) according to claim 1, optionally together with at least one storage-stable module each of B), C), D) and/or E) according to claim 15, is prepared and optionally stored, the modules being separately prepared, and the individual prepared modules are mixed together as required in quantities such that the solids content arising therefrom, 20 relative to the total solids content of the coating compositions, assumes the following percentages:

25

binder modules A): 5 - 99 wt.%  
colour modules B): 0 - 60 wt.%  
30 effect modules C): 0 - 50 wt.%  
crosslinking modules D): 0 - 50 wt.%  
rheological modules E): 0 - 50 wt.%

35 wherein the sum of the percentages should amount to 100%.

3. Modular system and process according to claim 1 or 2, characterised in that the binder module A) contains 10-99 wt.% of the cationically stabilised (meth)acrylic copolymer, 2-70 wt.% of the cationically stabilised polyurethane resin and 0.2-60 wt.% of the cationically stabilised (meth)acrylated polyurethane resin, wherein the stated percentages relate to the total binder solids content in the binder module and should add up to 100%.

10 4. Modular system and process according to one of the preceding claims, characterised in that the colour modules B) and effect modules C) each contain at least 10 wt.% of water.

15 5. Modular system and process according to one of the preceding claims, characterised in that one or more cationically stabilised (meth)acrylic copolymers with an OH value of 30 to 200, a number average molecular weight ( $M_n$ ) of 1000 to 200000 and an amine value of 15 to 150 are used.

20 6. Modular system and process according to one of claims 1 to 4, characterised in that one or more cationically stabilised polyurethane resins with a number average molecular weight ( $M_n$ ) of 3000 to 200000 and an amine value of 15 to 120 are used.

25 7. Modular system and process according to one of claims 1 to 4, characterised in that one or more cationically stabilised (meth)acrylated polyurethane resins with an amine value of 5 to 150 and an OH value of 0 to 150 are used.

8. Modular system and process according to one of the preceding claims, characterised in that the binder modules have a pH value of 5 to 7.
- 5 9. Modular system and process according to one of the preceding claims, characterised in that the crosslinking modules contain one or more melamine resins and/or blocked or unblocked polyisocyanates.
- 10 10. Modular system and process according to one of the preceding claims, characterised in that the rheological modules contain polymer microparticles, inorganic phyllosilicates and/or associative thickeners.
- 15 11. Modular system and process according to claim 10, characterised in that the associative thickeners used are one or more cationic associative thickeners based on polyurethane resins with hydrophilic segments in the main chain and hydrophobic segments on the chain ends, with an amine value of 5 to 100 and an OH value of 0 to 70.
- 20 12. Process according to one of the preceding claims, characterised in that the total solids content of the coating composition is adjusted to 10 to 80 wt.% at application viscosity.
- 25 13. Process according to claim 12, characterised in that aqueous effect base lacquers, single-tone aqueous base lacquers, aqueous single-coat topcoat lacquers and/or aqueous clear lacquers are produced using the same binder modules.
- 30 35 14. Process according to claim 2, 12 or 13, characterised in that an aqueous effect base lacquer is produced

with a proportion, in accordance with the solids content defined in claim 2, of:  
binder module of 10 to 99 wt.%,  
colour module of 0 to 40 wt.%,  
5 effect module of 0.01 to 50 wt.%,  
crosslinking module of 0 to 40 wt.%,  
rheological module of 0.01 to 50 wt.%,  
wherein the solids content of the coating composition  
is adjusted to 10 to 55 wt.% at application viscosity.

10

15. Process according to claim 2, 12 or 13, characterised in that a single-tone aqueous base lacquer is produced with a proportion, in accordance with the solids content defined in claim 2, of:  
binder module of 5 to 60 wt.%,  
colour module of 1 to 60 wt.%,  
crosslinking module of 0 to 40 wt.%,  
rheological module of 0 to 40 wt.%,  
wherein the solids content of the coating composition  
is adjusted to 10 to 60 wt.% at application viscosity.

20

16. Process according to claim 2, 12 or 13, characterised in that an aqueous single-coat topcoat lacquer is produced with a proportion, in accordance with the solids content defined in claim 2, of:  
binder module of 5 to 60 wt.%,  
colour module of 0.5 to 60 wt.%,  
effect module of 0 to 50 wt.%,  
crosslinking module of 0.5 to 40 wt.%,  
30 rheological module of 0 to 40 wt.%,  
wherein the solids content of the coating composition  
is adjusted to 10 to 70 wt.% at application viscosity.

35

17. Process according to claim 2, 12 or 13, characterised in that an aqueous clear lacquer is produced with a proportion, in accordance with the solids content defined in claim 2, of:

binder module of 15 to 90 wt.%,  
colour module of 0 to 20 wt.%,  
effect module of 0 to 10 wt.%,  
crosslinking module of 0.01 to 50 wt.%,  
5 rheological module of 0 to 40 wt.%,  
wherein the solids content of the coating composition  
is adjusted to 10 to 80 wt.% at application viscosity.

18. Aqueous coating compositions produced using the  
10 process of one of claims 2 to 17.

**Abstract:**

Modular system for the production of aqueous coating compositions, containing

- A) at least one aqueous binder module containing one or more cationically stabilised water-dilutable (meth)acrylic copolymers and cationically stabilised water-dilutable polyurethane resins and/or cationically stabilised water-dilutable (meth)acrylated polyurethane resins, optionally combined with non-ionically stabilised water-dilutable binders, water, optionally together with organic solvents and/or conventional lacquer additives, together with at least one of the following modules:
- ~~B) one or more colour modules containing water, coloured pigments and/or extenders and cationically stabilised paste resins, at least 6 wt.% of water, optionally together with water-dilutable cationically and optionally non-ionically stabilised binders, organic solvents and/or conventional lacquer additives, and/or~~
- C) one or more effect modules containing water, effect pigments, at least 6 wt.% of water, cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may optionally be present combined with further cationically or non-ionically stabilised water-dilutable binders, optionally together with organic solvents and/or conventional lacquer additives and/or

- D) one or more crosslinking modules containing one or more crosslinking agents, optionally together with organic solvents, water and/or conventional lacquer additives,  
and/or
- E) one or more rheological modules containing one or more organic and/or inorganic rheological control agents, optionally together with cationically, or cationically and non-ionically and/or non-ionically stabilised water-dilutable binders and/or organic solvents and/or water.

EXHIBIT

D

# United States Patent [19]

Falcoff et al.

[11]

4,403,866

[45]

Sep. 13, 1983

## [54] PROCESS FOR MAKING PAINTS

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[58] Field of Search 73/53; 366/132, 136, 366/137, 138, 142, 143, 145, 152, 159, 160, 177, 179, 182, 184

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## ABSTRACT

An apparatus and process for automatically and rapidly making a paint having the color values of a standard paint; a computer is used which is connected to and controls a multiplicity of metering pumps that are each individually connected to a supply of components used to make the paint such as binder solution, solvent and colorants; the components are accurately metered into a mixing vessel and mixed; paint is circulated through a recycle loop attached to the vessel; the loop contains a cell having a viewing window through which the paint is pumped, a colorimeter views the cell and determines the color values of the wet paint and feeds these values back to the computer which compares the values to values of the standard paint and calculates the amount of colorant to be added and signals the metering pumps to add colorant, the process is repeated until the paint is brought within the tolerance values of the standard paint.

20 Claims, 1 Drawing Figure

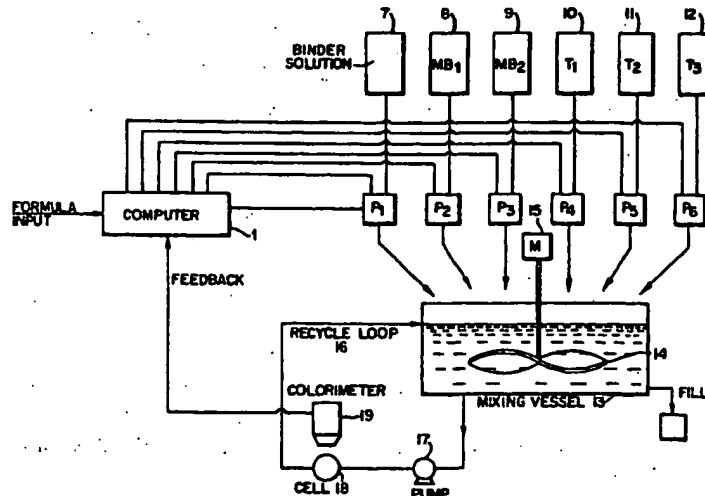
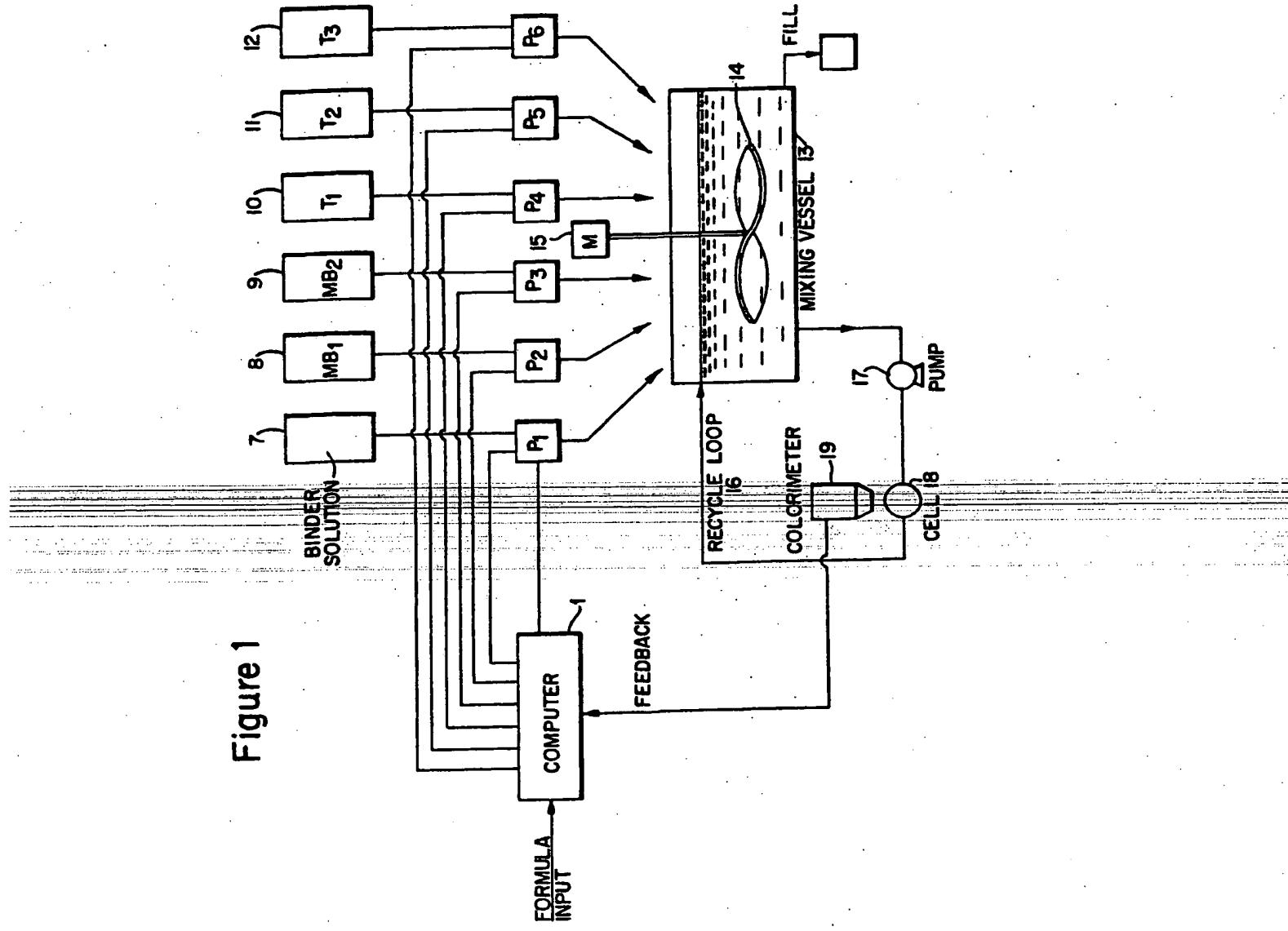


Figure 1



## PROCESS FOR MAKING PAINTS

## BACKGROUND OF THE INVENTION

This invention is related to a process and apparatus for making paints that match a standard paint.

Early devices such as those illustrated in Logan et al. U.S. Pat. No. 2,923,438 issued Feb. 2, 1960 provided a method for making paints according to a given formula but did not provide means for color matching the paint to a standard except for visual color matching using estimated additions of colorants to match a standard.

McCarty U.S. Pat. No. 3,601,589, issued Aug. 24, 1971, and McCarty et al. U.S. Pat. No. 3,916,168, issued Oct. 28, 1975, are directed toward computer controlled methods for preparing paints but use the standard procedure of spraying panels with paint, baking the panels and measuring color value of the panels and calculating and reshading the paint to bring the paint within acceptable color tolerance values.

British Pat. No. 1,589,705, published May 20, 1981, describes a general process for making a paint and adjusting the color values of the paint to come within the color tolerance values of a standard paint. However, this method directly utilizes light scattering and optical absorption properties of colorants used in the paints in combination with reflectance values of the paint at several wavelengths to determine the quantity of colorants required to bring the paint within an acceptable standard. When this procedure is used with the equipment disclosed in the patent, it does not provide for accurate color matching of a paint to a standard color and does not lend itself to a totally automated paint matching process.

There is a need for a process and apparatus that automatically, rapidly and accurately dispenses and mixes binder, solvents and colorants for a paint based on a standard formula, measures color values of the paint and shades the paint to within color tolerance values for that paint. The process and apparatus of the invention accomplish the above.

## SUMMARY OF THE INVENTION

An apparatus and process for making a paint that matches the color values of a standard liquid paint; the process utilizes the following: a computer electrically connected to a multiplicity of metering pumps, each pump is individually connected to a supply of a component used in the paint, the components used in the paint are liquid containing binder for the paint, solvent for the paint and colorant in the form of a dispersion or solution; a vessel that contains mixing means and a recycle loop; a pump that is tubularly connected to the vessel positioned in the recycle loop; a cell having a viewing window that is positioned in the recycle loop; a colorimeter having means to determine  $L^*$ ,  $a^*$  and  $b^*$  values of the paint that is positioned to view the window of the cell and that is electrically connected to the computer; the entire process is controlled by the computer and has the following steps:

- (1) providing the computer with
  - (a) formula of the paint to be made,
  - (b)  $L^*$ ,  $a^*$  and  $b^*$  values of the liquid standard paint,
  - (c) tolerance values of  $L^*$ ,  $a^*$  and  $b^*$  for the paint;
- (2) metering exact amounts of components of the paint into the mixing vessel by the metering pumps which are controlled by the computer;

- (3) mixing the components to form a paint;
- (4) circulating the paint through the cell at a uniform shear rate;
- (5) measuring and determining the  $L^*$ ,  $a^*$  and  $b^*$  values of the paint by the colorimeter;
- (6) transmitting said  $L^*$ ,  $a^*$  and  $b^*$  values to the computer;
- (7) determining color vectors of each colorant used to formulate the paint by adding a known amount of each colorant and for each addition repeating steps (3)-(6) and determining change in  $L^*$ ,  $a^*$  and  $b^*$  values;
- (8) comparing by the computer the  $L^*$ ,  $a^*$  and  $b^*$  values of the paint to the  $L^*$ ,  $a^*$  and  $b^*$  values of the standard paint and calculating the difference between the values of the paint and the standard paint and calculating the quantity of components to be added to the paint to bring the paint within  $L^*$ ,  $a^*$  and  $b^*$  tolerance values of the paint; and
- (9) repeating Steps (2)-(6) and (8) at least once in the event the paint is not within the  $L^*$ ,  $a^*$  and  $b^*$  tolerance values for the paint to bring the paint within said tolerance values.

If the color vectors for the colorants used to formulate the paint have been predetermined, the vectors are provided to the computer in Step (1) and Step (7) is omitted from the process.

## BRIEF DESCRIPTION OF THE DRAWING

The FIGURE shows a schematic diagram of the process of this invention used to make paints that match a standard paint.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of this invention makes a paint having color values that accurately match the color values of a standard without manual calculations or additions of colorants or without operator intervention. This makes the process particularly attractive for use in a distribution center which supplies a large number of paint colors or for use in a paint plant manufacturing process.

In reference to the FIGURE, a digital computer 1 is provided. Typical computers that can be used are Intel SBC 8010B Micro-computer, National Semiconductor BLC 8014 Micro-computer or an Intel SBC 80 20 Micro-computer.

The formula for the paint which includes the amount of colorants, binder and optional solvents that are required to make a certain volume of a batch of paint is fed into the computer. The  $L^*$ ,  $a^*$  and  $b^*$  values for the standard liquid paint and  $L^*$ ,  $a^*$  and  $b^*$  tolerance values for the paint that is to be made are fed into the computer. If the color vector values of the colorant solution or dispersion are unknown, the color vector values of the colorant are generated by the computer by measuring the  $L^*$ ,  $a^*$  and  $b^*$  values of a paint before and after an addition of a known amount of colorant and making the necessary calculations. If the color vector values of the colorants are known, these values are also fed into the computer so that the computer can calculate the amount of colorant that is required to bring the paint within color tolerance.

The color technology used in the process is well known and is fully discussed in F. W. Billmeyer and M. Saltzman, *Principles of Color Technology*, John Wiley and Sons, New York, 2nd Edition, (1981). Of particular interest is an article by A. B. J. Rodrigues in Fifth Inter-

national Conference in Organic Coatings Science and Technology Proceedings, Vol. 3, *Advances in Organic Coatings Science and Technology Series, "Theory and Implementation of Modern Techniques of Color Conception, Matching and Control"*, p. 272-282, (1979) which is hereby incorporated by reference.

The color of the paint is described in  $L^*$ ,  $a^*$  and  $b^*$  values which are coordinates in visual uniform color space and are related to  $X$ ,  $Y$  &  $Z$  tristimulus values by the following equations which have been specified by the International Committee on Illumination:

$L^*$  defines the lightness axis

$$L^* = 116(Y/Y_0)^{1/4} - 16$$

$a^*$  defines the red green axis

$$a^* = 500[(X/X_0)^{1/4} - (Y/Y_0)^{1/4}]$$

$b^*$  defines the yellow blue axis

$$b^* = 200[(Y/Y_0)^{1/4} - (Z/Z_0)^{1/4}]$$

where

$X_0$ ,  $Y_0$  and  $Z_0$  are the tristimulus values of the perfect white for a given illuminant;

$X$ ,  $Y$  and  $Z$  are the tristimulus values for the color.

The color vectors for each of the colorants used to prepare the paint are provided and determined as discussed above. The color vector is the movement in color space, i.e., the change in the  $L^*$ ,  $a^*$  and  $b^*$  values caused by the addition of a unit amount of each colorant used. For example,

$$\text{the color vectors for a color} = \begin{bmatrix} \frac{\partial L^*}{\partial C_1} & \frac{\partial L^*}{\partial C_2} & \frac{\partial L^*}{\partial C_3} \\ \frac{\partial a^*}{\partial C_1} & \frac{\partial a^*}{\partial C_2} & \frac{\partial a^*}{\partial C_3} \\ \frac{\partial b^*}{\partial C_1} & \frac{\partial b^*}{\partial C_2} & \frac{\partial b^*}{\partial C_3} \end{bmatrix}$$

where  $C_1$ ,  $C_2$  and  $C_3$  are the concentration of pigment or tint used in the color.

The metering pumps used in the process are electrically connected to and controlled by the computer and are tubularly connected to the components used to make the paint. The metering pumps preferably are computer controlled servo motor driven piston pumps. Computer controlled servo motor driven gear pumps can also be used. These computer controlled pumps can be programmed to be self-calibrating to insure accurate delivery of amounts of components used in the paint.

Referring to the FIGURE, metering pump  $P_1$  is tubularly connected to a supply of the binder solution 7,  $P_2$  is connected to a supply of a mill base 8 which is a pigment dispersion,  $P_3$  to a second mill base 9,  $P_4$  to a tinting solution 10,  $P_5$  to a second tinting solution 11 and  $P_6$  to a third tinting solution 12.

The components used to make the paint are metered into a mixing vessel 13 containing a mixer 14 having a mixing blade attached to a shaft and driven by a motor 15. The components are thoroughly mixed and circulated through a tubular recycle loop 16 by pump 17. Cell 18 for viewing the paint is connected in the recycle loop. It is preferred to use a variable speed mixer which is controlled by the computer to provide for sufficient mixing of each batch of paint and insure that mixing of the paint does not entrain air into the paint which causes a color shift in the wet paint.

The cell has a viewing window which is a medium that is transparent to the visible light spectrum and usually is made of quartz glass. Paint deposits can build-

up on the window of the cell which results in inaccurate readings. The paint flow through the cell should be at a uniform shear rate to provide a constant interface that can be measured by the colorimeter 19 and at a sufficient velocity to prevent a build-up on the cell window. The color values of paints containing metallic flake pigments are particularly difficult to measure since the metallic flake pigments must be in alignment in a plane parallel to the surface of the window of the cell to obtain constant readings by the colorimeter.

The paint flow through the cell should be within the laminar flow region and have a Reynold's Number of at least 25 and preferably about 100 but should not be over 2000. Paint flow within this range of Reynolds Numbers provides for sufficient flow so that the cell will be self cleaning and prevents a paint build-up on the window. The paint flow at the cell window is laminar and allows for the aforementioned alignment of metallic flake pigments to provide for accurate color analysis of the paint.

A Reynold's Number is a dimensionless quantity that measures flow and is well known in the art. Assuming a circular cross sectional area for the channel where the paint flows through the cell, the Reynold's Number is  $(4W)/(\pi DU)$  where  $W$  is the weight ratio of paint flow in grams/second,  $D$  is the diameter of the opening in centimeters and  $U$  is the viscosity of the paint in grams/centimeters second. When the cross sectional areas for the channel is not circular, the equivalent diameter is 2 times the square root of the cross sectional area divided by  $\pi$ .

A typical cell that can be used is disclosed in McKinney and Reilly U.S. Pat. No. 3,020,795, issued Feb. 13, 1962. Other cell designs can be used provided that the paint flows over the cell viewing window at the aforementioned Reynolds No. One solution to the problem of paint build-up on the cell window is the use of a fluorocarbon polymer coated quartz glass window in the cell. Also, an automatically activated wiper can be used to wipe the window of the cell before a reading is taken with the colorimeter.

Often the color shifts in a paint when the temperature of the paint changes. In a typical paint mixing process, the temperature of the paint increases and the paint should be cooled before the paint passes through the cell. To maintain the paint at a constant temperature, a conventional heat exchanger using chilled water for cooling can be used. Preferably, the heat exchanger is positioned before the cell to insure a constant temperature of the paint passing through the cell.

The colorimeter used in the process is electrically connected to the computer and preferably determines the  $L^*$ ,  $a^*$  and  $b^*$  values of the paint being prepared and feeds these values back to the computer. The colorimeter views the paint through the visible light spectrum of 400-700 nanometers (nm) for example, at 20 nm increments and calculates the  $L^*$ ,  $a^*$  and  $b^*$  values for the paint based on this data. It is possible to feed process signals from the colorimeter generated by viewing the paint to the computer and have the computer determine the  $L^*$ ,  $a^*$  and  $b^*$  values.

The computer takes these  $L^*$ ,  $a^*$  and  $b^*$  values and determines the difference between the  $L^*$ ,  $a^*$  and  $b^*$  values of the paint being prepared and tolerance values for the standard paint ( $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$ ). With the color vector information of the colorants and the  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$ , the computer determines the amount of

each of the colorants that is to be added to bring the paint within the tolerance values for the paint and activates the metering pumps which feed colorants into the mixing vessel. The above procedure, commonly called shading, is repeated until the paint being prepared is within  $L^*$ ,  $a^*$  and  $b^*$  tolerance values of the paint.

After the paint is prepared, it can be filled into suitable containers either automatically or manually by using conventional filling equipment and procedures.

After a first batch of paint has been prepared, multiple batches of the same paint can be formulated without using the aforementioned shading procedure. This is accomplished by mixing the same quantity of each of the components used to formulate the paint that were used in the first batch.

Instruments can be included in the process which measure properties such as the hiding power of the paint, the viscosity and density of the paint. The data generated by these instruments is fed to the computer and calculations are made and additions of binder solution, solvents and colorants are adjusted to bring the paint within tolerances for the above properties.

The process can be used in a paint manufacturing process as well as for making small batches of paint in a paint distribution center. In a manufacturing process, the automatic feedback from the colorimeter to the computer can be eliminated. The  $L^*$ ,  $a^*$  and  $b^*$  values determined by the colorimeter can be manually fed into the computer at an appropriate time in the manufacturing process. The computer calculates the amounts of solvents, binder solution and colorants to be added to bring a batch of paint within the desired tolerances and the additions are made manually or automatically. With the small batch process, the computer generally is used to control additions solvents, binder solution and colorants to the paint being prepared.

It is possible to determine  $L^*$ ,  $a^*$  and  $b^*$  values of a color from a color styling simulator as disclosed in Lee, U.S. Pat. No. 4,048,493 issued Sept. 13, 1977 and either feed these values automatically or manually into the computer. The process then prepares a paint having the desired  $L^*$ ,  $a^*$  and  $b^*$  values. Generally, a color stylist using a color styling simulator to develop a paint color for an automobile or a truck can work with a wide range of color tolerances. Therefore, the difference between the color of the wet paint and the dry paint and the relationship between the color of the image projected on the simulator and the color of the resulting object are not significant. A stylist is able to develop an acceptable color on the simulator and feed the  $L^*$ ,  $a^*$  and  $b^*$  values of the color into the process of this invention and obtain an acceptable paint. One practical use for such a system would be to have a customer who desires to refinish an auto or truck choose a color on the styling simulator and have the paint made immediately to specification.

It is possible to determine a spectral curve of a color with a spectrophotometer and feed these values into the computer which contains a program which generates a paint formula from the curve. The process of this invention is then used to prepare a paint that matches the color. The aforementioned technique can be used to match a dry color or the color of a wet paint sample that has an unknown formula.

The computer can be programmed to direct and control the preparation of a multiplicity of paints. For example, the computer can be given five paint formulas. After the preparation of each paint, the system automati-

cally washes the mixing vessel and recycle loop with an appropriate solvent and then the next paint is manufactured.

The following Example illustrates the invention. All parts and percentages are on a weight basis unless otherwise indicated.

#### EXAMPLE

A process as illustrated in the FIGURE was used to formulate a paint. A National Semiconductor BLC 80/10B, a computer controlled multispeed mixer driven via a Fairchild Corp. Model T-5800 Digital-to-Pneumatic Transducer and a colorimeter that has excellent repeatability were used in the process.

A dark blue acrylic lacquer was formulated. The standard lacquer has the following values. The following paint values were supplied to the computer:

(wet paint)	$L^* = 9.10$	$a^* = 8.72$	$b^* = -27.47$
(dry paint)	$L^* = 6.74$	$a^* = 9.79$	$b^* = -27.40$

Tolerance values for  $L^*$ ,  $a^*$  and  $b^*$  are  $\pm 0.3$ .

The following starting formula was given to the computer:

Titanium dioxide white pigment dispersion	33.5
Carbon black dispersion	71.8
Phthalocyanine green pigment dispersion	126.6
Phthalocyanine blue pigment dispersion	1557.0
Clear acrylic resin solution	7983.0
Total	9771.9

The above constituents were thoroughly mixed and color measurements are made. 30.3 grams of the white pigment dispersion was added and color measurements made which caused a color movement of  $\Delta L^* = 4.42$ ,  $\Delta a^* = 2.08$  and  $\Delta b^* = -3.48$ . These values are the white color vector values. Similarly, the green, black and blue color vector values were determined as above and the results are as follows:

	Amount added (grams)	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
Black	70.0	-0.99	-1.77	3.22
Green	106.0	-0.24	-2.28	2.25
Blue	530.0	-1.78	3.43	-1.17

Color measurements were made on the above paint after the above addition of white, black, green and blue dispersions and the following differences from the standard were calculated by the computer:

$$\Delta L^* = 0.05, \Delta a^* = 1.31 \text{ and } \Delta b^* = -1.95$$

Based on the above differences and the above color vector values, the computer calculated and dispensed the following and color measurements were made and differences from the standard were calculated:

Additions	(grams)
Carbon Black dispersion	39.4
Phthalocyanine green pigment dispersion	33.8

The color differences of the resulting paint from the above standard paint were determined and are as follows:

$$\Delta L^* = -0.17, \Delta a^* = -0.10 \text{ and } \Delta b^* = -0.19$$

These values are within the aforementioned tolerance values for  $L^*$ ,  $a^*$  and  $b^*$ .

The resulting paint was sprayed onto a primed steel panel and baked under standard conditions and the color values were determined and color differences of the dry paint from the above standard dry paint were calculated and are as follows:

$$\Delta L^* = 0.16, \Delta a^* = -0.16 \text{ and } \Delta b^* = -0.07$$

These values are within the aforementioned tolerance values for  $L^*$ ,  $a^*$  and  $b^*$ . An acceptable paint was formulated.

As a second example, a light salmon polyurethane enamel was formulated using the above process.

The standard enamel has the following values which were supplied to the computer:

$$\text{Wet paint } L^* = 79.54, a^* = 2.58 \text{ and } b^* = 6.28$$

Dry tolerance values for  $L^*$ ,  $a^*$  and  $b^*$  are  $\pm 0.2$ .

The following starting formula was provided to the computer:

(grams)

Yellow Iron Oxide Dispersion	10.4
Red Iron Oxide Dispersion	35.0
Carbon Black Dispersion	0.0
Titanium Dioxide White Pigment Dispersion	11258.6
Total	11304.5

The above constituents were thoroughly mixed and the following color difference from the standard were calculated.

$$\Delta L^* = 3.26, \Delta a^* = -2.04 \text{ and } \Delta b^* = -2.05$$

Color vectors for the above dispersions were predetermined and are as follows:

	Weight per 100 grams	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
Yellow Iron Oxide Dispersion	0.25	-0.46	-0.30	+2.69
Red Iron Oxide Dispersion	0.76	-1.09	+1.35	+0.15
Carbon Black Dispersion	0.11	-0.61	-0.14	-0.43
Titanium Dioxide White Pigment Dispersion	25.2	+0.58	-0.19	-0.67

Based on the above color differences and the above color vectors, the following additions of dispersions were calculated by the computer and these amounts were added and color differences from the standard enamel were calculated after each addition of pigment and dispersion:

Add	Amount Added (grams)	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
No. 1				
Yellow Iron Oxide Dispersion	57.2	0.24	0.51	0.25
Red Iron Oxide Dispersion	47.2			
No. 2				
Red Iron Oxide Dispersion	17.3	0.27	-0.27	-0.07
Carbon Black Dispersion	11.6			
Titanium Dioxide White Pigment Dispersion	2155.2			
No. 3				
Red Iron Oxide Dispersion	6.9	0.02	0.03	-0.07

After addition No. 3, the color differences were within the aforementioned tolerances values for  $L^*$ ,  $a^*$  and  $b^*$ .

The resulting paint was sprayed onto a primed steel panel and baked under standard conditions and the color values were determined and the color differences of the dry paint were calculated and are as follows:

$$\Delta L^* = 0.16, \Delta a^* = -0.16 \text{ and } \Delta b^* = -0.07$$

These values are within tolerance values and the paint was acceptable.

We claim:

1. A process for making a paint that matches the color values of a standard liquid paint, said process utilizes a computer electrically connected to a multiplicity of metering pumps, each pump being individually connected to a supply of a component used in the paint, said components used in the paint being liquid containing binder for the paint, solvent for the paint and colorant in the form of dispersions or solutions, a vessel containing a recycle loop and mixing means, a pump tubularly connected to the vessel positioned in a recycle loop, a cell having a viewing window positioned in the recycle loop, a colorimeter having means to determine  $L^*$ ,  $a^*$  and  $b^*$  values of the paint positioned to view the window of the cell and being electrically connected to the computer, said process being controlled by the computer comprises the following steps:

(1) providing the computer with

(a) formula of the paint,  
(b)  $L^*$ ,  $a^*$  and  $b^*$  values of the liquid standard paint,

(c) tolerance values of  $L^*$ ,  $a^*$  and  $b^*$  for the paint;

(2) metering exact amounts of components of the paint into the mixing vessel by the metering pumps which are being controlled by the computer;

(3) mixing said components to form a paint;

(4) circulating the paint through said cell at a uniform shear rate;

(5) measuring and determining  $L^*$ ,  $a^*$  and  $b^*$  values of the paint with the colorimeter;

(6) transmitting said  $L^*$ ,  $a^*$  and  $b^*$  values to the computer;

(7) determining color vectors of each colorant used to formulate said paint by adding a known amount of each colorant to the paint and for each addition

repeating Steps (3)–(6) and determining the change in  $L^*$ ,  $a^*$  and  $b^*$  values;

(8) comparing by the computer the  $L^*$ ,  $a^*$  and  $b^*$  values of the paint to the  $L^*$ ,  $a^*$  and  $b^*$  values of the standard paint and calculating the difference between the values of the paint and the standard paint, and calculating the quantity of components to be added to the paint to bring the paint within  $L^*$ ,  $a^*$  and  $b^*$  tolerance values of the paint; and

(9) repeating steps (2)–(8) at least once in the event the paint is not within the  $L^*$ ,  $a^*$  and  $b^*$  tolerance values for the paint to bring the paint within these tolerance values.

2. The process of claim 1 in which the color vector values of each of the colorants are known and are provided to the computer in Step (1) thereby eliminating Step (7) of the process.

3. The process of claim 1 or 2 in which the paint is maintained at a constant temperature before entering the cell.

4. The process of claim 1 or 2 in which the paint is circulated through the cell at a flow having a Reynolds Number of at least 25.

5. The process of claim 1 or 2 in which the metering pumps are servo motor controlled piston pumps.

6. The process of claim 1 or 2 in which the metering pumps are servo motor controlled gear pumps.

7. The process of claim 4 in which one of the components of the paint contains metallic flake pigments.

8. The process of claim 4 which includes measuring devices that provide the computer with the hiding, viscosity and density values of the standard paint and means for measuring and adjusting the hiding, viscosity and density of the paint.

9. The process of claim 1 or 2 which includes a final step of automatically filling containers after said paint has been prepared.

10. The process of claim 1 or 2 in which the computer is programmed to automatically prepare a multiplicity of paints which includes a step of washing the vessel, 40

11. The process of claim 1 or 2 in which step (9), in which components are metered manually into the mixing vessel adding amounts of components as calculated in step (8).

12. The process of claim 1 or 2 in which a spectrophotometer which measures a spectral curve of a color sample is electrically connected to the computer which determine the  $L^*$ ,  $a^*$  and  $b^*$  values from the spectral curve and transmits these values to the computer and tolerance values are transmitted to the computer and the process prepares a paint within the  $L^*$ ,  $a^*$  and  $b^*$  tolerance values.

13. The process of claim 1 or 2 in which the  $L^*$ ,  $a^*$  and  $b^*$  values determined from a spectral curve of a color and tolerance values for the paint are transmitted to the computer and the process prepares a paint within tolerance values.

14. The process of claim 1 or 2 in which an operator determines a color by a color styling simulator which visually shows a color, provides  $L^*$ ,  $a^*$  and  $b^*$  value data, is electrically connected to the computer, trans-

mits such data to the computer and transmits tolerance values to the computer and the process prepares a paint within the  $L^*$ ,  $a^*$ ,  $b^*$  tolerance values.

15. An apparatus for making paint that matches the color of a standard paint which comprises:

- (1) a computer;
- (2) individual vessels each containing components used in making paints, said components being liquid containing binder for the paint and colorant in the form of dispersions or solutions;
- (3) a multiplicity of metering pumps tubularly connected to the vessels containing components for said paint and electrically connected to and controlled by the computer;
- (4) a vessel containing mixing means into which the components for the paint are fed and mixed;
- (5) a tubular recycle loop attached to the vessel in which paint is removed from the vessel and circulated back into the vessel;
- (6) a pump positioned in the recycle loop for pumping paint through the loop;
- (7) a cell having a viewing window positioned in the recycle loop and designed to provide a uniform film of liquid paint on the viewing window; and
- (8) a colorimeter positioned to view the window of the cell electrically connected to the computer and having means to determine  $L^*$ ,  $a^*$  and  $b^*$  values of the paint;

wherein the computer is provided a formula of the paint, the  $L^*$ ,  $a^*$  and  $b^*$  values of a standard paint, tolerance values of  $L^*$ ,  $a^*$  and  $b^*$  for the paint, and is provided with or determines color vectors of the colorant dispersion or solutions; in making the paint the metering pumps controlled by the computer charge exact

amounts of components used in the paint into the mixing vessel, the components are mixed in the vessel and circulated through the recycle loop and the cell in the loop, the colorimeter views the paint through the cell window and determines the  $L^*$ ,  $a^*$  and  $b^*$  values of the paint, the values are fed to the computer which compares these values to the values for the standard paint and calculates the difference between the values of the paint and the standard paint and calculates the quantity of each component to be added to the paint to bring the paint within the tolerance  $L^*$ ,  $a^*$  and  $b^*$  values of the paint and in the event the paint is not within said tolerance values repeats at least once the procedure for making the paint until the paint is within the predetermined tolerances of  $L^*$ ,  $a^*$  and  $b^*$  values of the paint.

16. The apparatus of claim 15 which contains means for maintaining the paint at a constant temperature before the paint flows through the cell.

17. The apparatus of claim 15 in which the metering pumps are servo motor controlled piston pumps.

18. The apparatus of claim 15 which includes means for measuring and adjusting the hiding, viscosity and density of the paint.

19. The apparatus of claim 15 which includes means for filling containers after the paint is made.

20. The apparatus of claim 15 in which the metering pumps are servo motor controlled gear pumps.

EXHIBIT E



US005521234A

**United States Patent [19]****Brown et al.****[11] Patent Number: 5,521,234****[45] Date of Patent: May 28, 1996****[54] FLUIDIZED POLYMER SUSPENSION (FPS)  
FOR CONTINUOUS COATING  
COMPOSITION MANUFACTURE****[75] Inventors:** Richard G. Brown, Wilmington, Del.; Charles L. Burdick, Landenberg, Pa.; Charles W. Vanderslice, Newark, Del.**[73] Assignee:** Aqualon Company, Wilmington, Del.**[21] Appl. No.:** 235,056**[22] Filed:** Apr. 29, 1994**Related U.S. Application Data****[63] Continuation of Ser. No. 857,987, Mar. 26, 1992.****[51] Int. Cl.<sup>6</sup>** C08L 1/26; C08K 3/32; C08K 3/30; C08K 3/26**[52] U.S. Cl.** 524/44; 524/42; 524/43; 524/46; 524/416; 524/423; 524/425; 106/171; 106/177; 106/194; 106/197.1; 106/197.2**[58] Field of Search** 524/42, 44, 46, 524/43, 416, 423, 425; 106/171, 194, 177, 197.1, 197.2**[56]****References Cited****U.S. PATENT DOCUMENTS**

4,283,229	8/1981	Ging et al.	.....	106/171
4,883,536	11/1989	Burdick	.....	106/194
4,883,537	11/1989	Burdick	.....	106/194
5,028,263	7/1991	Burdick	.....	524/401

**Primary Examiner—Paul R. Michl****Assistant Examiner—LaVonda R. DeWitt****Attorney, Agent, or Firm—David Edwards****[57]****ABSTRACT**

A Fluidized Polymer Suspension (FPS) thickener comprising a hydroxyethylcellulose and/or alkyl or arylalkyl hydrophobically modified hydroxyethylcellulose added continuously to an aqueous dispersion increases productivity for manufacture of aqueous coating compositions. The FPS can be stored and metered without delays associated with dry powders. A latex paint is continuously produced by simultaneously or sequentially mixing latex binder, dispersed pigment and FPS thickener along with other ingredients.

**12 Claims, No Drawings**

**FLUIDIZED POLYMER SUSPENSION (FPS)  
FOR CONTINUOUS COATING  
COMPOSITION MANUFACTURE**

This application is a continuation of application Ser. No. 07/857,987, filed Mar. 26, 1992.

**FIELD OF THE INVENTION**

The invention relates to aqueous coating compositions which contain a water soluble polymer as a thickener. In particular the invention relates to manufacture of a coating composition where the thickener is incorporated as a Fluidized Polymer Suspension (FPS).

**BACKGROUND OF THE INVENTION**

U.S. Pat. No. 4,283,229 (Girg et al.) discloses that stable suspensions of nonionic cellulose ethers can be prepared in a solution of 4 to 12% electrolyte if alumina is added to the suspension. Prior art aqueous fluid suspensions of water soluble polymers are further described in U.S. Pat. Nos. 4,883,536 and 4,883,537. U.S. Pat. No. 4,883,536 covers the use of ammonium salts such as diammonium sulfate (DAS), diammonium phosphate (DAP), and ammonium polyphosphate for preparing fluid suspensions of water soluble polymers. U.S. Pat. No. 4,883,537 covers the use of concentrated aqueous potassium carbonate for preparing suspensions of sodium carboxymethylcellulose.

**SUMMARY OF THE INVENTION**

It is an object of the invention to provide a process for continuous manufacture of aqueous coating compositions for paint wherein a Fluidized Polymer Suspension (FPS) containing a thickener or thickener combination is used for rapid viscosity adjustment and ease of handling.

This process for producing an aqueous coating composition containing latex binder, pigment, and nonionic cellulose ether comprises simultaneously mixing a latex binder, dispersed pigment, and a fluidized polymer suspension of a hydroxyalkylcellulose or an alkyl or arylalkyl hydrophobically modified cellulose ether in an amount sufficient to prepare a coating composition.

Preferred thickeners are hydroxyethylcellulose (HEC) and hydrophobically modified hydroxyethylcellulose (HMHEC) containing an alkyl or arylalkyl group where the hydroxyethylcellulose has a Degree of Polymerization (D.P.) of from 800 to 4000, a hydroxyethyl Molar Substitution (M.S.) of 1.5 to 4.5 and a hydrophobe Degree of Substitution (D.S.) of from 0.001 to 0.01.

**DETAILED DESCRIPTION OF THE INVENTION**

It has been discovered that productivity in the manufacture of aqueous coating compositions comprising a latex binder, pigment, and a thickener can be significantly increased relative to the use of powdered materials, when an FPS containing a hydroxyalkylcellulose or a hydrophobically modified cellulose ether is added either batchwise or continuously. Hydroxyethylcellulose represents a hydroxyalkylcellulose which is widely used in the paint industry as a thickener. Hydrophobically modified cellulose ethers have come to be known as associative thickeners owing to their properties of enhanced viscosification provided by the associative behavior of hydrophobes chemically bound to a cellulose polymer. Assignee's copending patent applica-

tions, Ser. Nos. 428,912 and 701,756 disclose an arylalkyl hydrophobically modified hydroxyethylcellulose which provides improved leveling and sag resistance in a latex paint.

Due to the time required for hydration and dissolution of a powdered cellulosic polymer in waterborne paint, continuous production of paint, utilizing dry water-soluble celluloses, is not advantageous as compared to the novel use of FPS for the same result. The more rapid dissolution rates of FPS versus the dry material are also a benefit in batch paint production where residence time in the mixing chamber can be reduced significantly.

The following detailed experimental procedures were used in the examples which demonstrate the practice of the invention.

15 A 5-inch ID stainless steel vessel, with a  $\frac{1}{2}$ -inch diameter exit port and metal cuff on the bottom, was clamped to a support and the shaft and 2-inch diameter blade of a high speed impeller were inserted into the vessel to within  $\frac{1}{4}$ -inch of the bottom of the vessel. The blade was slightly off center in the vessel while the exit port was centered in the bottom of the vessel. The exit port of the vessel was fitted with a tube with an in-line flow rate control. Two large glass reservoirs were clamped to a support above the vessel; the reservoirs were fitted with tubes which reached into the vessel and which had flow rate control in-line. A peristaltic pump was fitted with tubing which reached into the stainless steel vessel and into a reservoir containing Natrosol® FPS-Plus 330 fluidized polymer suspension (available from Aqualon). One reservoir above the steel vessel was filled with Component 1 and the other with Component 2 (see Table 1). Flow rates were adjusted so that Component 1 entered the vessel at 9.75 grams per minute; Component 2 was introduced at 10 grams per minute, and Component 3 was added at 0.375 grams per minute. Impeller speed was approximately 2500 rpm (peripheral speed of 1310 feet per minute). After the flow rates were adjusted and the liquid level had risen to several inches above the blade, material was allowed to exit through the port in the bottom of the vessel at a rate equal to the combined addition rates of all three components. The material which exited was the finished product and was compared to the batch production control.

Continuous production can involve either simultaneous or sequential addition of ingredients.

45 The batch production control paint was prepared by simply adding each paint ingredient, one at a time, to a vessel equipped with a high-speed impeller. The order of addition was typical of batch paint production in which the water-soluble polymer, present as the rheology control agent, was dispersed in glycols and the pigment was dispersed in this fluid medium before the bulk of the ingredients were added to "let down" the paint. In this case, the water-soluble polymer was added in the form of an FPS, and pigment was added as a  $TiO_2$  slurry.

55 Initial viscosity, as well as the viscosity of paints which had aged overnight, were determined on a Stormer Viscometer at 200 rpm. Viscosity data are reported in Kreb Units in Table 2. Weight percent cellulosic thickener is also reported and is based on the total weight of  $FPSS \times 0.25$  (FPS is 20-25% wt. % polymer, depending on type) divided by total weight of paint  $\times 100$ . High shear viscosity was determined on an ICI cone and plate viscometer at  $12,000s^{-1}$ . Leveling was determined using a Leneta Leveling Test Blade and Drawdown Levelness Standards. Sag resistance was measured using a Leneta Anti-Sag Meter. Spatter resistance testing was conducted by rolling out paint on a vertical surface above a black panel.

Spatter patterns were compared to Gardner/Sward standards appearing in the 13th Edition of the ASTM Paint Testing Manual (STP 500). Specular gloss at 60° was measured using a BYK Labotron Gloss Unit.

Delta E (color development) values were based on measurement of color parameters using a Brightimeter over drawn down and "rubbed-up" areas on the unsealed portion of a test chart. Scrub resistance testing was conducted using ASTM Method D2486.

The invention has industrial applicability for the manufacture of paints. The examples illustrate both batch and continuous paint making processes without being limiting.

#### Procedure A

##### Preparation of Natrosol® FPS-Plus 330

A fluidized-polymer suspension of Natrosol® Plus 330 HMHEC was prepared in concentrated aqueous diammonium sulfate (DAS) solution for evaluation as a paint thickening agent. To prepare the suspension as a first step, 0.2 parts by weight of Kelzan® S xanthan gum was dissolved in 60.5 parts by weight water with two hours stirring. After the xanthan had dissolved, 14.2 parts by weight of DAS was added to the solution and stirred to dissolve. After the DAS had dissolved, 25 parts by weight of Natrosol® Plus 330 HMHEC was added to the solution and stirred briefly to disperse. As a final step, 0.1 parts by weight of Proxel® GXL preservative was added to the suspension with stirring. The final product was a pourable fluid suspension designated Natrosol® FPS-Plus 330.

#### Procedure B

##### Preparation of Natrosol® FPS-G

A fluidized-polymer suspension of Natrosol® 250GR HEC was prepared for evaluation as a paint thickening agent. To prepare the suspension in the first step, 1 part by weight of CMC-7L1T was dissolved in 59.7 parts of water with 30 minutes stirring. After this 14.2 parts by weight of diammonium phosphate (DAP) was added to the water and stirred to dissolve. After the CMC and DAP were completely dissolved, 25 parts by weight of Natrosol® 250GR HEC was added to the solution and stirred to disperse. As a final step, 0.1 parts by weight of Proxel GXL® preservative was added to the suspension with stirring. The end product was observed to be a pourable fluid suspension designated Natrosol® FPS-G.

#### Procedure C

##### Preparation of Natrosol® FPS-HB

A fluid suspension of Natrosol® 250 HBR HEC was also prepared in a different manner for evaluation as a paint thickener. In the first step of preparation, 0.2 parts by weight of Kelzan® S xanthan gum was dissolved in 47.8 parts by weight of water with 2 hours stirring. After the xanthan was dissolved, 0.9 parts by weight of Lomar® D condensed naphthalene sulfonate was added to the water and stirred to dissolve. Following this, 0.1 parts by weight of Hercules® Defoamer SGL was added to the water and then 30 parts by weight of sodium formate was added to the water and stirred to dissolve. Once the sodium formate had dissolved, 20 parts by weight of Natrosol® 250HBR HEC was added to the water and stirred briefly to disperse. After this, 0.9 parts by weight of Alipal® CO-433 was added to the mixture and

stirred briefly to disperse. As a final step, 0.1 parts by weight of Proxel® GXL was added as a preservative to the suspension and stirred briefly. The resulting product was observed to be a pourable fluid suspension designated Natrosol® FPS-HB.

#### Procedure D

##### Preparation of Natrosol® FPS-MB

A fluidized polymer suspension of Natrosol® 250MBR HEC was prepared with identical methodology and ingredients as described in the previous example above only in this case Natrosol® 250MBR HEC was substituted for Natrosol® 250HBR HEC. A pourable fluid suspension was obtained in this case designated Natrosol® FPS-MB. This product was evaluated in paint.

#### Procedure E

##### Preparation of Natrosol® FPS-Plus 430

A fluidized polymer suspension of Natrosol® Plus 430 HMHEC was prepared in concentrated aqueous sodium formate for use in paint making. To prepare the suspension, 0.16 parts by weight of Kelzan® S xanthan gum was first dissolved with two hours stirring in 56.74 parts by weight of water. After the xanthan had dissolved, 28 parts by weight of sodium formate was dissolved in the water with brief stirring. Once the sodium formate had dissolved, 25 parts by weight of Natrosol® Plus 430 HMHEC were added to the solution and stirred to disperse. As a final step, 0.1 parts by weight Proxel® GXL preservative was added to the suspension. The final product, designated Natrosol® FPS-Plus 430, was observed to be fluid and pourable. This product was evaluated in paint.

#### EXAMPLE 1

##### Interior Semigloss Continuous Production

A Fluidized Polymer Suspension (FPS) polymer system for thickening and rheology control was used to thicken a semigloss paint in a continuous process utilizing all liquid components. The paint formulation was a slightly modified version of a published formulation and was based on a vinyl-acrylic latex. Paint ingredients were divided into two blended components and a third component which consisted of a Fluidized Polymer Suspension (FPS). All liquid materials were used including a titanium dioxide slurry. The compositions of the three components are listed in Table 1.

TABLE 1

##### CONTINUOUS PAINT MAKING COMPONENTS

Material	Grams
<u>Component 1</u>	
Ucar® 367	934.00
Texanol®	40.00
Nopco® NDW	6.00
Propylene Glycol	54.10
Total	1034.10
<u>Component 2</u>	
Propylene Glycol	135.90
Tamol® 731	23.00
Triton® N-57	2.66
Nuosept® 95	2.00

TABLE 1-continued

CONTINUOUS PAINT MAKING COMPONENTS	
Material	Grams
Nopco® NDW	4.00
Triton® GR-7M	2.00
Ti-Pure® R-940 Slurry	666.66
Water	232.00
AMP-95™	2.66
Total	1070.88
Component 3	
Natrosol® FPS-Plus 330 (see Procedure A)	39.44
Formulation Constants	
PVC = 22.4%	
NVW = 48.9%	
Initial Viscosity = 88 KU	

The two blended components and the FPS were metered simultaneously into a stainless steel vessel which was equipped with a high speed impeller and outlet port. Blended components were added, by gravity feed, at 9.75 grams per minute (Component 1) and 10 grams per minute (Component 2). FPS (Component 3) was added 0.375 grams per unit using a peristaltic pump. Addition rates were adjusted so as to keep the paint composition constant over the course of paint production and the ingredients in proper proportion relative to one another. Paint was removed from the vessel at a rate equal to the combined component addition rates. As a control, the same paint formula was prepared in a typical batch process.

The properties of the paints produced by both continuous and batch processes are listed in Table 2.

TABLE 2

PAINT PROPERTIES FOR CONTINUOUS AND BATCH PROCESSES

Property	Process:	
	Continuous	Batch
KU ION*	88/95	85/91
Weight % Thickener	0.46	0.46
HSV (ICI, Ps)	1.1	1.1
Leveling	3	2
Sag	22	24
Spatter	9	8
Gloss (60°)	56	59
Delta E	0.6	0.5
Scrub, cycles	>1600	>1600

\*ION = Initial/Overnight

This example shows that continuous paint manufacture with FPS yields the same quality paint as with a batch paint process. Continuous paint manufacture is only possible with FPS and not dry cellulosic polymer.

#### EXAMPLE 2

##### Interior Flat Batch Production

The interior flat paint, shown in Table 3 was prepared using a high-speed disperser and vessel. Water, KTPP dispersant, R & R 551® water-dispersible lecithin dispersant, Tamol® 731 dispersant (Rohm and Haas), Hercules® SGL defoamer, ethylene glycol wet-edge agent, and Carbitol®

acetate coalescing solvent were sequentially added to the mixing vessel with the disperser operating at low speed (~1400 ft/minute). The Ti-Pure® R-901 titanium dioxide pigment, Camel CARB® calcium carbonate pigment, Iceberg® clay pigment, and Imsil® 1160 silica pigment were then charged in order to the vessel and the speed increased to ~4000 ft/minute. The let-down was conducted by adding the Makon® 10 surfactant, Polyco® 2161 vinyl acrylic latex and Proxel® GXL can preservative with thorough mixing until a smooth uniform base paint resulted. It has been found that the FPS can be added as well to the pigment dispersion before let-down or at virtually any stage of manufacture.

A 200 g portion of the base paint (Table 3) was thickened by adding 5.41 g of Natrosol® FPS-Plus 330 (25 wt. % Natrosol® Plus 330 HMHEC) and 49.59 g of water with moderate stirring on a propeller stirrer. A second sample of base paint was thickened by adding 38.25 g of a 4 wt. % aqueous solution of the same lot of Natrosol® Plus 330 HMHEC and 16.75 g of water with stirring. The resulting paints were evaluated using standard paint testing techniques. The initial Stormer viscosities of these two paints were found to be 94 and 95 KU, respectively. The weight percent dry thickener levels (thickening efficiencies) on total paint were, respectively, 0.53% and 0.60%. Comparative application properties were as follows:

TABLE 3

FLAT BASE PAINT FORMULATION						
Material	Parts by Weight					
Water	1350.0					
KTPP	13.5					
Ross & Rowe 551®	13.5					
Tamol® 731	33.8					
Hercules® SGL Defoamer	13.5					
Ethylene Glycol	135.5					
Carbitol® Acetate	67.5					
Ti-Pure® R-901	1181.3					
Camel CARB®	1012.5					
Iceberg® Clay	843.8					
Imsil® 1160	168.8					
Let Down						
Makon® 10	20.3					
Polyco® 2161	1350.0					
Proxel® GXL	3.4					
Total	6207.4					
Thickener Form	Leveling Index	Anti-Sag Index	Brushing Viscosity	Spatter Resistance	Contrast Ratio	Color Dev.
FPS Solution	3	15	1.1	9	0.985	0.88
	3	16	1.2	9	0.982	1.25

Level scale: 10=perfect leveling; 0=extremely poor leveling. Anti-sag Index: 24=no sag; 4=extreme sag.

Brushing Viscosity: measured in poises on an ICI viscometer.

Spatter Resistance: 10=no spatter; 0=extreme spatter.

Contrast Ratio: measured at 3-mils wet after drying.

Color Development: measured as color difference.

60

#### EXAMPLE 3

##### Interior Flat Batch Production

A 200 g aliquot of the interior flat base paint, shown in Table 3, was thickened with 5.48 g of Natrosol® FPS-HB (20 wt. % Natrosol® 250 HBR HEC) and 49.5 g of water to

an initial Stormer viscosity of 96 KU. A second equivalent portion was thickened with 38.25 g of a 3 wt. % aqueous solution of the same Natrosol® 250-HBR HEC lot and 16.75 g of water. The resulting Stormer viscosity was 95 KU. Relative percent thickening efficiencies were 0.43 and 0.45%, respectively. The applied properties of each paint were as follows:

Thickener Form	Leneta Leveling	Anti-Sag Index	Brushing Viscosity	Spanner Resistance	Contrast Ratio	Color Dev.	10
FPS Solution	3	10	0.9	2	0.986	0.95	

15.

#### EXAMPLE 4

##### Interior Semigloss Batch Production

By the same paint-making technique illustrated in Example 2 above, the interior semigloss base paint shown in Table 4 was prepared. A 235 g portion of this semigloss base paint was then thickened with 3.85 g of Natrosol® FPS-MB (20 wt. % Natrosol® 250 MBR HEC) and 36.15 g of water to a Stormer viscosity of 88 KU. A second portion was thickened with 24.75 g of a 4 wt. % aqueous solution of the same Natrosol® 250 MBR HEC lot and 15.25 g of water. The initial Stormer viscosity was 89 KU. Relative weight percent thickening efficiencies were 0.28 and 0.36%, respectively. Comparative application properties are shown below:

Thickener Form	Leneta Leveling	Anti-Sag Index	Brushing Viscosity	Spanner Resistance	60° Gloss	Color Dev.	35
FPS Solution	4	24	2.1	1	39	2.37	

40.

#### EXAMPLE 5

##### Exterior Flat Batch Production

The exterior flat house paint formulation shown in Table 5 was prepared by the same paint-making technique described above in Example 2.

TABLE 4.

SEMIGLOSS BASE PAINT FORMULATION		50
Material	Parts by Weight	
Propylene Glycol	542.5	
Tamol® SG-1	57.7	
Hercules® SGL Defoamer	13.6	55
Ti-Pure® R-900	1627.5	
Imsil® A-15	169.6	
<u>Let Down</u>		
Rhoplex® AC-417	3390.6	
Hercules® SGL Defoamer	18.4	60
Propylene Glycol	67.9	
Texanol®	146.5	
Proxel® GXL	6.8	
Triton® GR-7M	3.5	
Water	140.5	
<u>Total</u>	6184.8	65

TABLE 5

EXTERIOR FLAT BASE PAINT	
Material	Parts by Weight
Water	720.0
Foamaster® VL	6.0
Ethylene Glycol	167.4
Tamol® 8-850	63.0
KTPP	9.0
Triton® CF-10	15.0
Ti-Pure® R-902	1620.0
Horsehead® XX-503R	300.0
Minex™ 4	900.0
Disperse to Hegman 6 on a high-speed disperser and let-down as follows:	

##### Let Down

Rhoplex® AC-64	2291.4
Foamaster® VL	18.0
Texanol®	69.6
Scane® M-8	9.0
<u>Total</u>	6188.4

A 245 g portion of exterior flat base paint was thickened with 5.46 g of Natrosol® FPS-G (25 wt. % Natrosol® 250 GR HEC) and 33.94 g of water to an initial Stormer viscosity of 93 KU. A second aliquot was thickened using 12.32 g of a 12 wt. % aqueous solution of the same Natrosol® 250GR HEC lot and 27.08 g of water. The initial Stormer viscosity was 92KU. Weight percent thickening efficiencies were, respectively, 0.48 and 0.52%. Comparative application properties were as follows:

Thickener Form	Leneta Leveling	Anti-Sag Index	Brushing Viscosity	Spanner Resistance	Color Dev.
FPS Solution	1	24	1.0	3	0.42

#### EXAMPLE 6

##### Interior Flat Batch Production

The interior flat base paint shown in Table 6 was prepared according to the procedure described in Example 2.

TABLE 6

INTERIOR FLAT BASE PAINT	
Material	Parts by Weight
Water	1760.0
Ethylene Glycol	64.0
Tamol®	64.0
Colloid® 643	12.8
Proxel® GXL	6.4
AMP-95™	6.4
Tamol® 731	32.0
Makon® 10	19.2
Ti-Pure® R-931	800.0
ASP® 170	640.0
ASP® 400	640.0
Camel-CARB®	832.0
Disperse to Hegman 3-4 on a high-speed disperser and let-down as follows:	
<u>Let Down</u>	
UCAR® 367	1152.0

##### Let Down

TABLE 6-continued

INTERIOR FLAT BASE PAINT	
Material	Parts by Weight
Colloid ® 643	12.8
Total	6041.6

A 230 g sample was thickened with 4.03 g of Natrosol® FPS-Plus 430 (25 wt % Natrosol® Plus 430 HMHEC) and 45.97 g of water to an initial Stormer viscosity of 97 KU. A second portion was thickened using 33.60 g of a 3 wt % solution of the same Natrosol® Plus 430 HMHEC lot and 16.40 g of water. The initial Stormer viscosity was 96 KU. The thickening efficiency was 0.36% in both cases. Paint application properties are compared below:

Thickener Form	Leneta Leveling	Anti-Sag Index	Brushing Viscosity	Spatter Resistance	Color Dev.
FPS	6	10	0.7	7	0.80
Solution	7	11	0.7	7	0.29

## EXAMPLE 7

## Interior Semigloss Batch Production

A 24.8% pigment volume concentration (PVC), 32.9% nonvolatiles by volume (NVV), semigloss formula, based on an all-acrylic latex, Rhoplex® AC-417 was used. The pH of the paint is 8.4. The formula is shown in Table 2. Base paint (300 grams), containing all paint ingredients except thickener and additional let-down water, was placed in a beaker on a torque transducer apparatus. The base paint was stirred with an H-blade stirrer at 1000 rpm. The torque, measured by the transducer and indicative of the viscosity of the paint, was followed as a function of time and was plotted on a strip chart recorder. In the case of dry polymer addition, 49.42 grams of water, followed by 1.58 grams of dry Natrosol® Plus 330 HMHEC was added to the stirring base paint. In the case of FPS, 44.68 grams of water and 6.32 grams of a fluidized polymer suspension containing 25 wt % of the same Natrosol® Plus 330 HMHEC lot was added. The weight percent thickener in both paints was 0.45%. The semigloss paint thickened with the dry polymer did not achieve maximum viscosity (indicative of complete thickener dissolution) until 35 minutes had elapsed from the time of thickener introduction. The paint thickened with the fluidized polymer suspension achieved maximum viscosity in 20.5 minutes. In the case of the dry polymer, the maximum torque reading achieved was 32 units, while in the case of the FPS, the maximum torque reading was 40 units. This represents a 41.4% increase in speed of dissolution and 25% increase in thickening efficiency. These data are contained in Table 7.

Examples 2-6 demonstrated the utility of FPS for paint making to be equivalent to that of solutions of cellulosic polymers. Example 7 shows the benefit of FPS over dry cellulosic polymer for enhanced rate of paint production in a batch process.

TABLE 7

TORQUE (VISCOSITY) VS. TIME READINGS DRY NATROSOL ® PLUS 330 VS. FLUIDIZED VERSION OF NATROSOL ® PLUS 330 IN SEMIGLOSS PAINT			
	Dry Natrosol ® Plus 330 HMHEC	Fluidized Natrosol ® Plus 330 HMHEC	
10	Time (minutes)	Torque (viscosity)	Time (minutes)
	0.0	0.0	0.0
	1.0	0.0	0.2
	2.0	2.5	0.4
	3.0	6.0	0.5
	4.0	9.0	1.0
	5.0	12.0	1.5
	7.0	16.0	2.5
	10.0	20.0	3.5
	12.0	23.0	4.5
	14.0	24.0	5.5
	17.0	26.0	6.5
	20.0	27.5	7.5
	25.0	29.0	8.5
	30.0	31.0	9.5
	35.0	32.0	10.5
	40.0	32.0	15.5
	45.0	32.0	20.5
25			25.5
			40.0

## EXAMPLE 8

## Flat Batch Production

A 62.7% PVC, 31.3% NVV formula based on a vinyl-acrylic latex (Polyco® 2161) was utilized. The pH of the paint is 7.2. The formula is shown in Table 3.

Base paint (250 grams), containing all paint ingredients except thickener and additional let-down water was placed in a beaker on a torque transducer apparatus. The base paint was stirred with an H-blade stirrer at 1000 rpm. The torque, measured by the transducer and indicative of the viscosity of the paint, was followed as a function of time and was plotted on a strip chart recorder. In the case of dry polymer addition, 65.72 grams of water, followed by 1.91 grams of dry Natrosol® Plus 330 HMHEC was added to the stirring base paint. In the case of FPS, 60.00 grams of water and 7.62 grams of a fluidized polymer suspension containing 25 wt % of the same Natrosol® Plus 330 HMHEC was added. The weight percent thickener in both paints was 0.60%. The flat paint thickened with the dry polymer did not achieve maximum viscosity (indicative of complete thickener dissolution) until 65 minutes had elapsed from the time of thickener introduction. The paint thickened with the fluidized polymer suspension achieved maximum viscosity in 7.5 minutes. In the case of the dry polymer, the maximum torque reading achieved was 44 units, while in the case of the FPS, the maximum torque reading was 56 units. This represents a 88.5% increase in speed of dissolution and 27% increase in thickening efficiency. These data are contained in Table 8.

TABLE 8

TORQUE (VISCOSITY) VS. TIME READINGS  
DRY NATROSOL® PLUS 330 VS. FLUIDIZED VERSION  
OF NATROSOL® PLUS 330 IN FLAT PAINT

Dry Natrosol® Plus 330 HMHEC	Fluidized Natrosol® Plus 330 HMHEC		
Time (minutes)	Torque (viscosity)	Time (minutes)	Torque (viscosity)
0.0	0.0	0.0	0.0
10.0	0.0	0.2	5.0
15.0	0.0	0.4	9.0
20.0	0.0	0.5	12.0
25.0	1.0	1.0	30.0
30.0	4.0	1.5	42.0
35.0	13.0	2.5	47.0
40.0	35.0	3.5	50.0
45.0	38.0	4.5	54.0
50.0	41.0	5.5	56.0
55.0	43.0	6.5	57.0
60.0	43.0	7.5	56.5
65.0	44.0	8.5	55.0
70.0	44.0	9.5	55.0
75.0	44.0	10.5	55.0
80.0	32.0	15.5	55.0
85.0	32.0	20.5	55.0
		25.5	55.0

Higher throughput, either in batch or continuous production, results from faster dissolution rates of the FPS versus the dry polymer. The important parameter is how fast thickened paint achieves its maximum or "plateau" viscosity. Higher thickening efficiency is demonstrated in the same experiments. The same amount of thickener is added to the paint on an active basis and the paint thickened with FPS displays a higher viscosity than the paint thickened with the dry polymer. In batch production, the polymer is completely dissolved in a given volume of paint or paint components before the product is finished and packaged. In continuous paint production, the residence time of the paint ingredients in a mixing chamber is dependent on the speed with which the thickener dissolves. The viability of continuous paint production utilizing the FPS was demonstrated.

## EXAMPLE 9-10

## Improved Scrub Resistance

The paints in Example 2 were tested in accordance with ASTM Method D2486, "Scrub Resistance of Interior Latex Flat Wall Paints." As shown below, the sample thickened with Natrosol® FPS-HB had superior scrub resistance:

Thickener Form	Scrub Resistance (cycles to failure)	Increase (%)
FPS Solution	661 472	40 —

Paints like those described in Example 5 were similarly tested in accordance with ASTM Method D2486. The data below demonstrate the superior scrub resistance obtained with the Natrosol® FPS-Plus 430-thickened paint versus the sample thickened with the solution polymer.

Thickener Form	Scrub Resistance (cycles to failure)	Increase (%)
FPS Solution	560 390	43.5 —

The above two examples are not meant to limit the potential scrub improvements offered by other FPS products.

What is claimed is:

1. A process for continuously producing an aqueous coating composition containing latex binder and pigment comprising preparing an aqueous fluidized polymer suspension (FPS) of a conventional nonionic cellulose ether or an alkyl or arylalkyl hydrophobically modified cellulose ether where the hydrophobically modified cellulose ether is one or more of cetyl modified hydroxyethylcellulose, nonylphenyl modified hydroxyethylcellulose, nonylphenyl modified ethyl hydroxyethylcellulose, or alkyl glycidyl ether modified hydroxyethylcellulose and further where the hydroxyethylcellulose or ethylhydroxyethylcellulose is hydrophobically modified with a degree of substitution (D.S.) of from 0.001 to 0.01 by dissolving in water at least one salt selected from the group consisting of potassium carbonate, potassium bicarbonate, diammonium sulfate, diammonium phosphate, sodium formate, and dibasic potassium phosphate to form a salt solution and then suspending the polymer in said salt solution to form a pourable fluid suspension and continuously dispersing the suspension in the latex binder and pigment in an amount sufficient to form the aqueous coating composition.
2. The process of claim 1 where the alkyl hydrophobically modified cellulose ether is cetyl modified hydroxyethylcellulose.
3. The process of claim 1 where additional ingredients selected from the group consisting of a preservative, a defoamer, a dispersant, a coalescing solvent, calcium carbonate, titanium dioxide, silica, a surfactant, and kaolin clay are added to prepare an aqueous latex paint.
4. The process of claim 3 where the fluidized polymer suspension contains a hydroxyalkylcellulose.
5. The process of claim 4 where the hydroxyalkylcellulose is hydroxyethylcellulose.
6. The process of claim 5 where the hydroxyethylcellulose has a Degree of Polymerization (D.P.) of from 800 to 4000.
7. The process of claim 1 where the FPS further contains a xanthan gum.
8. The process of claim 1 where the FPS contains a low molecular weight polysaccharide as a suspending agent.
9. The process of claim 8 where the low molecular weight polysaccharide is carboxymethylcellulose (CMC).
10. A process for producing an aqueous coating composition containing latex binder, pigment and nonionic cellulose ether comprising continuously and simultaneously or sequentially mixing a latex binder, dispersed pigment and a fluidized polymer suspension of an alkyl or arylalkyl hydrophobically modified cellulose ether where the arylalkyl hydrophobically modified cellulose ether is nonylphenyl modified hydroxyethylcellulose in an amount sufficient to prepare the aqueous coating composition, wherein the fluidized polymer suspension is prepared by dissolving in water at least one salt selected from the group consisting of potassium carbonate, potassium bicarbonate, diammonium sulfate, diammonium phosphate, sodium formate, and dibasic potassium phosphate to form a salt solution and then suspending the polymer in said salt solution to form a

**13**

pourable fluid suspension and continuously dispersing the suspension in the latex binder and pigment in an amount sufficient to form the aqueous coating composition.

11. The process of claim 10 where the alkyl hydrophobically modified cellulose ether is cetyl modified hydroxyethylcellulose.

**14**

12. The process of claim 10 where the hydrophobically modified cellulose ether is an alkyl glycidyl ether modified hydroxyethylcellulose.

\* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 5,521,234

DATED : May 28, 1996

INVENTOR(S) : Richard G. Brown, Charles L. Burdick & Charles W. Vanderslice

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 2, line 57, insert two spaces and replace "viscosity" with  
—Viscosity—.

Column 3, line 35, delete "e" on Natrosol.

Signed and Sealed this

Seventh Day of January, 1997

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

EXHIBIT  
K

## [54] TRAFFIC MARKING PAINT

[75] Inventor: Masao Kitano, Osaka, Japan

[73] Assignee: Toa Paint Co., Ltd., Osaka, Japan

[21] Appl. No.: 436,387

[22] Filed: Oct. 25, 1982

## [30] Foreign Application Priority Data

Oct. 29, 1981 [JP] Japan 56-174020

[51] Int. Cl.<sup>3</sup> C09D 5/00; C09D 3/48; E01F 9/04; E01F 9/08

[52] U.S. Cl. 523/172; 524/457; 524/476

[58] Field of Search 523/172; 260/998.19; 524/457, 476

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Primary Examiner—Melvyn I. Marquis

Assistant Examiner—Herbert J. Lilling

Attorney, Agent, or Firm—Armstrong, Nikaido, Marmelstein &amp; Kubovcik

## [57] ABSTRACT

A traffic marking paint having an excellent drying property comprising a non-aqueous resin dispersion, a filler and a pigment. The traffic paint can be used with or without glass beads, and can be quickly dried without remaining the inside portion of the coated paint layer in the undried state.

1 Claim, No Drawings

## TRAFFIC MARKING PAINT

## BACKGROUND OF THE INVENTION

The present invention relates to a traffic marking paint of non-aqueous dispersion type.

A traffic paint of non-aqueous dispersion type has the advantages that it is low in viscosity and high in solid content and can be quickly dried, and that a hydrocarbon solvent which is photochemically inert, is usable. However, the paint has the drawback that if it is thickly coated, a film is formed on the surface area due to quick drying and a solvent is hard to evaporate from the inside. In order to eliminate this drawback, it is proposed to incorporate about 20% by weight of glass beads in the paint, thereby securing the apparent quick drying property.

It is a primary object of the present invention to provide a traffic marking paint of a non-aqueous dispersion type having an excellent drying property without using glass beads.

This and other objects of the present invention will become apparent from the description hereinafter.

## SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a traffic marking paint comprising 10 to 40% by weight of a non-aqueous dispersion of a resin having a glass transition temperature of 20° to 70° C., 40 to 60% by weight of a filler, and a pigment.

The traffic marking paint of the invention can be quickly dried without remaining the inside portion of the coated paint layer in the undried state.

## DETAILED DESCRIPTION

The term "non-aqueous resin dispersion" as used herein means a dispersion in which a resin is dispersed in an organic solvent, unlike an aqueous latex or emulsion in which a resin is dispersed in water.

Non-aqueous dispersions of resins having a glass transition temperature of 20° to 70° C. are usable in the invention. The non-aqueous dispersions are prepared by known processes, e.g. a process in which a dispersant such as an alkyd resin and a dispersoid such as an acrylic monomer are dissolved or dispersed in a dispersion medium such as an aliphatic hydrocarbon solvent and the polymerization is conducted, and a process in which the dispersant is first formed by polymerization and the dispersoid is then added to the reaction mixture and polymerized. In order to obtain non-aqueous resin dispersions suitable for attaining the objects of the invention, an aliphatic hydrocarbon such as hexane, heptane or cyclohexane and an aromatic hydrocarbon such as toluene or xylene are preferably employed in the invention as a dispersion medium. These mediums may be employed alone or in admixture thereof. Resins having a certain degree of reactivity are preferably employed as a dispersant, e.g. an acrylic resin such as polymethyl methacrylate, an alkyd resin, an acrylic modified alkyd resin, chlorinated rubber and polybutadiene. The dispersoid used in the invention includes ethylenically unsaturated monomers, e.g. acrylic monomers such as methyl acrylate or methacrylate, ethyl acrylate or methacrylate, butyl acrylate or methacrylate and 2-hydroxyethyl acrylate, acrylonitrile and styrene. The ethylenically unsaturated monomers may be employed alone or in admixture thereof. A mixture of methyl methacrylate and ethyl and butyl acrylates is preferably

employed in the present invention, and in particular, the mixture containing 20 to 70% by weight of methyl methacrylate is preferred.

Preferable non-aqueous dispersions are obtained by the polymerization of a monomer mixture containing methyl methacrylate in the aliphatic or aromatic hydrocarbon dispersion medium in the presence of the above-mentioned dispersant.

The non-aqueous dispersions preferably used in the present invention are those having a heating residue (solids content) of from 50 to 70% by weight and containing a polymer having a molecular weight of 10,000 to 20,000 and a glass transition temperature of 20° to 70° C. The ratio of the dispersoid to the dispersant is from about 70/30 to 80/20 by weight. It is important to adjust the monomer composition of the dispersoid so that the glass transition temperature of the polymer in the obtained dispersion falls within the above range. When the proportion of methyl methacrylate in the monomer mixture used as a dispersoid is made high, the glass transition temperature becomes high and the apparent drying rate of a coated paint becomes fast, but a film is hard to be formed and cracking is easy to occur. On the other hand, when the proportion of methyl methacrylate is decreased to lower the glass transition temperature, the film forming property is raised, but the drying property is remarkably lowered. Also, when the molecular weight of the polymer is far higher than the above range, the viscosity of the polymer increases and the stability of the paint is lowered. When the molecular weight is small, the film forming property tends to be improved, but the characteristics of non-aqueous dispersions are not effectively exhibited.

In addition to the non-aqueous resin dispersion, other resins compatible with the dispersion, such as alkyd resins, acrylic resins and chlorinated rubber may be employed in the present invention.

The non-aqueous dispersion is employed in an amount of 10 to 40% by weight based on the traffic marking paint.

Usual color pigments such as titanium dioxide and chrome yellow are employed in the present invention.

As a filler, there are preferably employed inorganic fine particles which are capable of imparting the hardness and the abrasion resistance to coatings so that the coatings possess the durability. Examples of the filler are, for instance, calcium carbonate, talc, silica sand, magnesium carbonate, dolomite, a glass powder, and the like. The filler is employed in an amount of 40 to 60% by weight based on the paint.

The traffic marking paint of the present invention may contain other usual paint additives, e.g. solvent, pigment dispersing agent, viscosity controller, coalescing agent and stabilizer.

The pigmentation is carried out by a usual grinding method, and for instance, a sand mill, a colloid mill, DYNOMILL (registered trademark of WILLY A. BACHOFEN AG, Swiss) and a dissolver are usable. The paint is prepared in a manner such as a manner in which the whole amounts of the components are admixed at one time and ground, and a manner in which a mill base is first formed by employing an alkyd resin or the like, and after grinding it, the non-aqueous dispersion is admixed therewith.

The traffic marking paint of the present invention has a viscosity of 90 to 140 KU measured by a Krebs-Stormer viscometer at 25° C. according to Japanese

Industrial Standard (JIS) K 5665-1981 and a heating residue of about 70 to about 90%.

The traffic paint may be employed with glass beads incorporated therein to provide a beaded reflecting paint. In that case, the glass beads may be previously incorporated in the paint upon preparing it.

The coating of the traffic paint of the present invention can be made in any known manners such as air spraying and airless spraying. The traffic paint may be coated at ordinary temperature, but the spraying of the paint heated to lower the viscosity at a temperature of not more than 80° C. is preferable, since the film formation is good and the paint can be coated in thick. In that case, a conventional hot marking car or heat spraying equipment can be directly used. In case of hot airless spraying, the spraying from a nozzle of 1.0 to 1.4 mm. in diameter at 80° C. in temperature of the paint and 80 to 110 kg./cm.<sup>2</sup> in spraying pressure is suitable. The spraying is conducted usually to give a coating having a thickness of 300 to 1,000 μm. in wet state and 200 to 600 μm. in dry state. When the thickness of the coating is less than the above range, the coating is insufficient in durability, and when the thickness is more than the above range, the inside portion of the coating is hard to be dried due to drying in the surface area.

The traffic paint of the present invention can be used as it is or with glass beads to provide a reflective coating. In case of providing a reflective coating by employing the traffic paint of the present invention, the so-called drop-in application system in which glass beads are incorporated in the sprayed paint being dropping from a spray nozzle is rather suitable than the so-called drop-on application system in which glass beads are scattered on the coated paint.

The present invention is more specifically described and explained by means of the following Examples in which all % and parts are by weight unless otherwise noted. It is to be understood that the present invention is not limited to the Examples and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

#### EXAMPLE 1

##### [Non-aqueous resin dispersion A]

Dispersoid: Acrylic polymer containing 45% of methyl methacrylate units

Dispersant: Alkyd resin

Dispersion medium: n-Heptane

Dispersoid/dispersant ratio: 70/30 by weight

Glass transition temp.: 35° C.

Heating residue: 60%

The above non-aqueous dispersion A was admixed with other additives according to the following formulation and the grinding was conducted by employing a colloid mill to give a traffic marking paint.

Components	Amount (part)
Non-aqueous dispersion A	18.0
Medium-oil alkyd resin	14.0
Rutile titanium dioxide	14.0
Calcium carbonate	51.5
Dispersion stabilizer	0.5
Cyclohexane	2.0
(Total	100.0)

#### EXAMPLE 2

##### [Non-aqueous resin dispersion B]

Dispersoid: Acrylic polymer containing 20% of methyl methacrylate units

Dispersant: Acrylic modified alkyd resin

Dispersion medium: n-Heptane

Dispersoid/dispersant ratio: 70/30 by weight

Glass transition temp.: 24° C.

Heating residue: 55%

A traffic marking paint was prepared according to the following formulation by employing a colloid mill.

Components	Amount (part)
Non-aqueous dispersion B	30.0
Medium-oil alkyd resin	3.0
Rutile titanium dioxide	14.0
Calcium carbonate	34.5
Dolomite	16.0
Dispersion stabilizer	0.5
n-Heptane	2.0
(Total	100.0)

#### EXAMPLE 3

##### [Non-aqueous resin dispersion C]

Dispersoid: Acrylic polymer containing 60% of methyl methacrylate units

Dispersant: Acrylic modified alkyd resin

Dispersion medium: n-Heptane

Dispersoid/dispersant ratio: 70/30 by weight

Glass transition temp.: 35° C.

Heating residue: 55%

A traffic marking paint was prepared according to the following formulation by employing a colloid mill.

Components	Amount (part)
Non-aqueous dispersion C	17.0
Medium-oil alkyd resin	16.0
Rutile titanium dioxide	14.0
Calcium carbonate	34.5
Dolomite	16.0
Dispersion stabilizer	0.5
Cyclohexane	2.0
(Total	100.0)

#### EXAMPLE 4

##### [Non-aqueous resin dispersion D]

Dispersoid: Acrylic polymer containing 15% of methyl methacrylate units

Dispersant: Acrylic polymer

Dispersion medium: Mixed solvent of n-heptane and toluene

Dispersoid/dispersant ratio: 80/20 by weight

Glass transition temp.: 18° C.

Heating residue: 50%

A traffic marking paint was prepared according to the following formulation by employing a colloid mill.

Components	Amount (part)
Non-aqueous dispersion D	30.0
Medium-oil alkyd resin	2.0

-continued

Components	Amount (part)
Rutile titanium dioxide	14.0
Calcium carbonate	51.5
Dispersion stabilizer	0.5
n-Heptane	2.0
(Total	100.0)

## EXAMPLE 5

## [Non-aqueous resin dispersion E]

Dispersoid: Acrylic polymer containing 70% of methyl methacrylate units

Dispersant: Acrylic modified alkyd resin

Dispersion medium: Mixed solvent of n-heptane and toluene (70/30 by volume)

Dispersoid/dispersant ratio: 70/30 by weight

Glass transition temp.: 79° C.

Heating residue: 60%

A traffic marking paint was prepared according to the following formulation by employing a colloid mill.

Components	Amount (part)
Non-aqueous dispersion E	16.0
Medium-oil alkyd resin	16.0
Rutile titanium dioxide	14.0
Calcium carbonate	34.5
Dolomite	16.0
Dispersion stabilizer	0.5
n-Heptane	2.0
(Total	100.0)

## EXAMPLE 6

## [Non-aqueous resin dispersion E]

Dispersoid: Acrylic polymer containing 60% of methyl methacrylate units

Dispersant: Acrylic modified alkyd resin

Dispersion medium: Mixed solvent of n-heptane and toluene (70/30 by volume)

Dispersoid/dispersant ratio: 70/30 by weight

Glass transition temp.: 35° C.

Heating residue: 55%

A traffic paint was prepared according to the following formulation by employing a dissolver.

Components	Amount (part)
Non-aqueous dispersion F	13.0
Medium-oil alkyd resin	12.0
Rutile titanium dioxide	15.0
Calcium carbonate	39.0
Glass beads	15.0
Dispersion stabilizer	1.0
Cyclohexane	5.0
(Total	100.0)

Yellow traffic paints were also prepared in the same manner as in the above Examples except that titanium dioxide was replaced by chrome yellow pigment.

In the above Examples in which there were employed non-aqueous dispersions of resins having different glass transition points, the alkyd resin was employed as a modifier to balance the drying property of the paints and physical properties of the obtained coatings. In case that the glass transition point was high, the alkyd resin was employed in a larger amount, and in case that the glass transition point was low, the alkyd

resin was employed in a smaller amount. A modifier such as alkyd resin, acrylic resin or chlorinated rubber should be employed in an amount smaller than the non-aqueous resin dispersion, since when the modifier is employed in an amount larger than the non-aqueous dispersion, the characteristics of the non-aqueous dispersion are lost.

The traffic paints of the present invention obtained in the above Examples and two kinds of conventional 10 alkyd resin traffic paints of heat spraying type (Comparative Examples 1 and 2) were tested according to JIS K 5665 "Traffic paint 2nd Class".

The results are shown in Table 1.

The testing methods are as follows:

Viscosity: JIS K 5665, item 5.5

Heating residue: JIS K 5665, item 5.19

Specific gravity: JIS K 5665, item 5.4

Appearance of coating: JIS K 5665, item 5.9

Drying time, no pick up: JIS K 5665, item 5.10, time till a paint does not stick to a tire

Whiteness: JIS K 5400, item 6.6, 45°-0° diffuse reflectance

Bleeding: JIS K 5665, item 5.13, 45°-0° diffuse reflectance

Water resistance: JIS K 5665, item 5.17, 24 hours

Alkali resistance: JIS K 5665, item 5.18, saturated solution of calcium hydroxide, 18 hours

Weather resistance: JIS K 5665, item 5.24, 12 months

Beads fixing rate: JIS K 5665, item 5.22

Abrasion resistance: JIS K 5665, item 5.15, 100 rotations

TABLE 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
<u>Non-aqueous dispersion</u>				
Glass transition point (°C.)	35	74	55	18
Properties of paint				
Viscosity (KU value at 25° C.)	110	100	100	95
Heating residue (%)	85	84	86	84
Specific gravity (at 20° C.)	1.65	1.66	1.68	1.65
<u>Properties of coating</u>				
Appearance	pass	pass	pass	pass
Drying time, no pick up (min.)	1	1.5	1	2.5
Thickness 10 mil	3	5	3	7
20 mil	7	10	6.5	>10
30 mil	91	92	90	88
Whiteness (reflectance)	87	89	86	84
Bleeding (reflectance)	pass	pass	pass	pass
Water resistance	"	"	"	"
Alkali resistance	"	"	"	"
Weather resistance	"	"	"	"
Beads fixing rate (over 90%)	140	120	140	180
Abrasion resistance (mg.)				
<u>Ex. 5</u> <u>Ex. 6</u> <u>Com. Ex. 1</u> <u>Com. Ex. 2</u>				
<u>Non-aqueous dispersion</u>				
Glass transition point (°C.)	79	35	—	—
Properties of paint				
Viscosity (KU value at 25° C.)	105	(35 poises at 20° C.)	125	95
Heating residue (%)	85	83	81	75
Specific gravity (at 20° C.)	1.66	1.90	1.77	1.60
<u>Properties of coating</u>				
Appearance	pass	pass	pass	pass
Drying time, no pick up (min.)	1	1	3	8
Thickness 10 mil	3	2	10	>10
20 mil	8	4	>10	>10
30 mil	91	90	86	85
Whiteness (reflectance)	89	87	81	78
Bleeding (reflectance)	pass	pass	pass	pass
Water resistance	"	"	"	"
Alkali resistance	"	"	"	"

TABLE 1-continued

Weather resistance	"	"	"	"
Beads fixing rate (over 90%)	"	"	"	"
Abrasion resistance (mg.)	280	70	230	250

The traffic paints of Examples 1 to 3 are far superior in drying property and abrasion resistance to conventional alkyd resin traffic paints of Comparative Examples 1 and 2, and these results show that the traffic paints of the present invention have an excellent practicability.

The traffic paint of Example 4 using a non-aqueous dispersion of a resin having a low glass transition temperature is somewhat slow in drying speed. The traffic paint of Example 5 using a non-aqueous dispersion of a resin having a high glass transition temperature is good in apparent drying property, but the film forming property is poor and it causes cracks on the surface of the coating.

The traffic paint of Example 6 in which glass beads are incorporated to provide a reflective coating, has an excellent drying property. Even if the paint was coated in wet thickness of 0.8 to 1.0 mm., it did not show the

phenomenon that the inside portion of the coated paint remained undried.

In addition to the components used in the Examples, other components can be used in the Examples as set forth in the specification to obtain substantially the same results.

What is claimed is:

1. A traffic marking paint comprising 10 to 40% by weight of a non-aqueous dispersion of a resin having a glass transition temperature of 20° to 70° C. and having a molecular weight of 10,000 to 20,000, 40 to 60% by weight of a filler, and a pigment, said paint having a solids content of 70 to 90% by weight, said non-aqueous dispersion having a solids content of 50 to 70% by weight and being prepared by polymerizing an ethylenically unsaturated monomer selected from the group consisting of methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, 2-hydroxyethyl acrylate, acrylonitrile and styrene in a dispersion medium in the presence of a dispersant selected from the group consisting of an acrylic resin, an alkyd resin, an acrylic modified alkyd resin, chlorinated rubber and polybutadiene, the ratio of said ethylenically unsaturated monomer to said dispersant being from about 70/30 to about 80/20 by weight.

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EXHIBIT  
G

# United States Patent [19]

Sperry et al.

[11]

4,243,430

[45]

Jan. 6, 1981

[54] PIGMENT DISPERSANT FOR AQUEOUS PAINTS

[75] Inventors: Peter R. Sperry, Doylestown; Richard J. Wiersema, North Wales, both of Pa.

[73] Assignee: Rohm and Haas Company, Philadelphia, Pa.

[21] Appl. No.: 835,262

[22] Filed: Sep. 21, 1977

[51] Int. Cl. 3 C08L 33/10

[52] U.S. Cl. 106/308 M; 106/308 Q; 106/309; 260/29.6 WB; 260/29.6 H; 260/29.6 M; 260/42.21

[58] Field of Search 106/308 M, 308 Q; 526/317; 260/29.6 RB, 29.6 RW, 29.6 WB, 29.6 H, 29.6 M, 42.21

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Primary Examiner—Jacqueline V. Howard  
Attorney, Agent, or Firm—Harold L. Greenwald

[57] ABSTRACT

Described herein is a pigment paste for use in an aqueous paint comprising a film-forming latex polymer, a pigment and a dispersant copolymer. Also described is the dispersant copolymer which serves the function of dispersing the pigment in the preparation of the paste and maintaining the dispersion in the paste and paint made therefrom. The dispersant copolymer is such that its complex salt formed with Zn++ and ammonia is water-soluble at a pH of 9.6. The dispersant is a copolymer of an  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid and at least one other ethylenically unsaturated monomer. The dispersant is particularly adapted to preparing paste for difficult-to-formulate paints such as paints with reactive pigments and paints requiring high levels of dispersant.

14 Claims, No Drawings

## PIGMENT DISPERSANT FOR AQUEOUS PAINTS

## BACKGROUND OF THE INVENTION

This invention concerns the improvement of pigment pastes, for use in aqueous coating compositions containing a film-forming latex polymer and a pigment, by incorporating into the paste a novel dispersant polymer of great versatility. The dispersant polymer is an effective dispersant for a wide range of pigments and useful in making a pigment paste therefrom; it is also an effective dispersant for the pigment in the presence of the other components of many coating compositions. For example, the dispersant does not appreciably affect the corrosion-resistance properties of a reactive pigment paint in which it is incorporated.

The use of low molecular weight polyelectrolytes as dispersing agents for pigments in water based coatings is known. U.S. Pat. No. 3,980,602 discloses dispersants containing 5 to 25% by weight of acrylic or methacrylic acid in polymers based on alkyl acrylates and certain alkyl methacrylates; styrene may be substituted for the latter. These polymers having weight average molecular weights in the range 500 to 30,000. Dispersants based on copolymers of olefins and maleic anhydride are disclosed in U.S. Pat. No. 2,930,775. Formulations containing these dispersants may often exhibit poor stability in the presence of divalent cations. U.S. Pat. No. 3,840,487 discloses acrylic polymer dispersants for high gloss paints the dispersants being composed of 40 to 95 mole percent unsaturated monocarboxylic acid, such as acrylic or methacrylic acid, and 5 to 60 mole percent unsaturated carboxylic acid esters, such as the esters of these acids. Average molecular weights below 75,000 are mentioned. British Pat. No. 985,276 discloses a pigment dispersant comprising acrylic acid, methacrylic acid, an ester of methacrylic acid and a monohydric alcohol and an ester of methacrylic acid and a polyhydric alcohol. The polymerization are in a aqueous medium and produce an emulsion copolymer. Canadian Pat. No. 655,884 discloses dispersants which are copolymers of methacrylic acid and esters of acrylic and methacrylic acids made by a process employing high levels of persulfate initiators such that sulfate groups, believed to be terminal on the polymer chain, are responsible for the enhanced dispersing activity recited for the polymers.

A pigment paste is a pigment concentrate made to permit substantial reduction with solvents, water or vehicle (paint components other than solid pigment) in the preparation of a paint. The pigment paste, also known as pigment dispersion, comprises pigment, dispersant, defoamer, water and/or a glycol and is used to formulate a latex paint. One common way of making latex paints is to charge the paste components to a dispersion mill in which the pigment is dispersed in the aqueous or glycol system and then "letdown" with the remainder of the paint constituents, normally comprising latex, thickener, water, and other specialized additives, often in the small mill running at lower speeds.

Pigments are normally supplied in the fine particle size necessary for use to form thin coating films. For use in paint, the particles must be thoroughly wetted and pigment agglomerates broken up in a high-speed disperser, sand mill or other dispersing equipment. Once a good pigment dispersion is obtained, it must be maintained through the process of paint manufacture and storage. The role of the dispersant is to aid in the disper-

sion of pigment and thus to develop the full value of hiding and color to be contributed by the pigment. The dispersant also aids in fluidizing the pigment slurry for ease of milling, increases the stability of the pigment suspension in water or glycol, or a mixture thereof, and finally the stability of the completed paint. In considering dispersants and pigment pastes made therefrom, many paint formulations present few difficulties, but if a dispersant is to be effective in a wide range of formulations it must perform well when used in the difficult-to-formulate paint systems. Often the performance of a dispersant and the pigment paste made therefrom is limited by there being a comparatively low top limit to the amount of dispersant which may be used without producing deleterious effects. Another factor which limits utility of many dispersants is incompatibility with the so-called reactive pigments, particularly those used in corrosion inhibiting paint formulations. Thus, such a paint formulation serves as an excellent screening system to demonstrate the versatility of dispersants for use in pigment pastes. The dispersant of the instant invention permits the formulation of pigment pastes containing reactive and corrosion inhibiting pigments which may be used to prepare paints very stable in the wet state and which deposit films imparting a high degree of corrosion resistance when dry. The dispersant of the instant invention permits the corrosion resistant property to be maintained even when used at high concentration in the paste. Thus, pastes made with the dispersant of this invention can be used to make paints which achieve a balance of high stability and high corrosion resistance as well as the many other desiderata of high quality paints.

## SUMMARY OF THE INVENTION

The pigment paste of this invention is adapted for use in a wide variety of aqueous latex paints, particularly difficult-to-formulate paints, such as paints containing reactive pigments, e.g., ZnO. The paste comprises a water compatible suspension of a finely divided pigment and, for dispersion of the pigment, an effective amount of the water soluble dispersant comprising the novel copolymer of this invention. The suspension medium is water or a water soluble compound such as an alcohol or a glycol. The dispersant polymer comprises a water soluble or base soluble addition copolymer of greater than about 30% by weight of an  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid and at least one other ethylenically unsaturated monomer. The copolymer has an average acid strength such that its apparent pKa lies between about 6.0 to 7.5. The copolymer is low in molecular weight, having a number average molecular weight between about 500 and about 15,000. The copolymer is further characterized by the fact that the salt formed when in combination with the zinc ammonia complex ion,  $Zn(NH_3)_4^{++}$ , is soluble in an aqueous system at a pH of 9.6.

## DETAILED DESCRIPTION

The most important ingredients of the pigment paste are the pigment itself, the dispersant and the medium. Typical pigments (primary pigments and extender pigments) are titanium dioxide and other titanium pigments, white lead, barium sulfate, calcium carbonate, lithopone, silica, talc, mica, clays, iron oxide, carbon black, cadmium sulfide, toluidene red, chrome orange, chrome yellow, chrome green and the so-called reac-

itive pigments which include multivalent metal compounds, such as lead silico-chromate, zinc chromate, calcium-zinc molybdate, barium metaborate, zinc oxide, and zinc sulfide. Other reactive and unreactive pigments are well known in the art. Preferred are those pastes comprising titanium dioxide and, for pastes containing reactive pigment, the reactive pigment zinc oxide.

The pastes are fluid pastes of high solids content and low medium content, usually an aqueous medium comprising water or water and minor or major proportion of an alkylene glycol such as ethylene glycol, propylene glycol, which is preferred, or hexylene glycol. The glycols function to slow the drying rate of a paint made from the paste and thus to increase wet-edge time and to improve levelling. The glycol may also have served as the medium during the polymerization of the monomers to form the copolymer of the dispersant. Dissolved in the medium may be a number of other components as discussed hereinbelow.

The dispersant comprises an addition copolymer, water soluble in alkaline aqueous medium, of over about 30% by weight of an  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid. As polymerizable  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acids, there are used acrylic acid, methacrylic acid, or other  $\alpha$ -substituted polymerizable acrylic acid, or itaconic acid. The preferred acids are methacrylic and then acrylic. In place of the free acids there may be used water-soluble salts thereof, including the ammonium salts and the alkali-metal salts such as lithium or potassium carboxylates. The salts may be preformed or they may be formed in the dispersion system. The necessary and important consideration is that carboxylate groups be supplied to enter into the copolymer. The best way to ensure that carboxylate groups do in fact enter into the copolymer chain is to use a free acid monomer.

The other ethylenically-unsaturated monomers employed in the copolymer are preferably mono-ethylenically unsaturated, thus the copolymers are preferably linear addition polymers. The most important of the monomers are the acrylic acid and methacrylic acid esters of an alcohol having 1 to 18 carbon atoms with 1 to 8 carbon atom alkyl methacrylates being preferred. Examples of the acrylates and methacrylates are methyl acrylate, ethyl acrylate, butyl acrylates, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylates, and butyl methacrylates, which are preferred. Other ethylenically unsaturated monomers include the vinyl esters of an aliphatic acid, having 1 to 18 carbon atoms, such as vinyl formate, vinyl propionate, and especially vinyl acetate and vinyl butyrate, mono-unsaturated hydrocarbons such as ethylene, propylene, isobutylene, styrene, chloroprene,  $\alpha$ -methylstyrene, and other substituted styrenes, vinyl chloride, vinylidene chloride, vinyl toluene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, vinyl 2-methoxy-ethyl ether, vinyl 2-chloroethyl ether and the like. The preferred monomers are styrene, acrylonitrile, vinyl acetate and especially the acrylate and methacrylate esters of aliphatic, cyclo-aliphatic or aromatic alcohols containing from 1 to 18 carbon atoms. These alcohols may also contain atoms other than carbon and hydrogen such as oxygen, sulphur, nitrogen, etc., as part of other functional groups such as ethers, alcohols, amides and the like. It is preferred that at least 30% by weight of the copolymer be a hydrocarbon monomer, a

$C_1-C_{18}$  ester of acrylic acid or of methacrylic acid, or a mixture of these. A more preferred composition has 50% to 70% by weight of  $C_1-C_8$  alkyl acrylate and/or methacrylate units in the copolymer. A still more highly preferred composition contains 60% to 65% by weight of the  $C_2-C_4$  alkyl acrylate and/or methacrylate units. The most preferred units are propyl and butyl methacrylate and acrylate units. In general, it is preferred that at least half of the ethylenically-unsaturated monomers other than the acid monomers in the copolymer be methacrylate or acrylate esters.

The dispersant copolymer is a copolymer of greater than about 30% by weight of the  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid, and is desirably not over 70% by weight of such acid. Preferably, the copolymer has 30% to 50% by weight of acid mer units with 35% to 40% being most preferred. The preferred acids are acrylic acid, methacrylic acid and itaconic acid, with methacrylic acid being the most preferred. 20 The water soluble copolymer of the dispersant is soluble in neutral water or in basic aqueous solutions. The copolymer also consists of mer units of at least one other ethylenically-unsaturated monomer. In most formulations the dispersant polymer is in water solution as the alkali metal (for example, sodium or potassium) ammonium amine (for example, triethylamine, dimethylamino-ethanol, 2-amino-2-methyl-1-propanol, triethanolamine, pyridine, morpholine) or the like, salt of the copolymer. The number average molecular weight of the copolymer is in the range of about 500 to about 15,000, preferably between 1,000 and 6,000, and most preferably between 2,000 and 4,000. The number average molecular weight is determined by osmometric methods well known in the art.

The copolymer has an apparent pKa between about 6.0 and about 7.5, preferably between 6.3 and 7.2, and most preferably between 6.5 and 7.0. The values are referred to as "apparent pKa" because unlike the base titration of simple acids in aqueous solution, where the pKa is comparatively independent of the fraction of the molecules neutralized, in the case of polymers the pKa often shows a marked dependence on the fraction neutralized. In this specification the "apparent pKa" refers to the pKa at half neutralization; this is essentially the same as the pH of the solution containing the half neutralized copolymer. The data are obtained by titration of the polymer in the acid form, using dilute base as the titrant, as is customary in acid-base titrations. Typical is the use of an automatic titrator such as the Radiometer Titrograph model SBR2C, using a 5 milliliter burette containing 0.50 M sodium hydroxide, set up to span the entire range from a pH of between 1 to 2 to a pH between 11 and 12 in about 8 minutes. In a typical determination, about 2 milliequivalents of the polymer are dissolved in 75 milliliters of 0.1 M sodium chloride solution. This polymer solution is acidified with a slight excess of 0.5 M hydrochloric acid and then back-titrated with 0.5 M sodium hydroxide. When the acid mer units in the polymer are mono-basic two vertical inflections appear in the titration curve produced by the instrument. The first inflection is the completion of titration of the strong acid, such as the added hydrochloric acid, present in the solution. The second vertical inflection represents the complete neutralization of the acid groups in the polymer. The apparent pKa is the pH of the solution midway (in titrant) between these inflections. In the case of a dibasic mer unit, in the polymer, a third vertical inflection may be observed, as is observed in the

titration of many simple dibasic acids, and two apparent pKa values may be assigned.

The dispersant polymer sample for titration is to be free of ammonia and amines; alternatively the titration curve is corrected for the presence of ammonia or amines using the technique common to the field of acid-based titration in analytical chemistry. One procedure is to remove the volatile base by adding excess sodium hydroxide and warming the solution while sparging with carbon dioxide-free nitrogen. A second procedure is to recognize the end point due to the amine or ammonia (using the known pKa of the amine or ammonia) and by the usual calculations correct for its presence.

An important characteristic of the copolymer is that it forms a water soluble salt with a zinc ammonia complex ion at a pH of 9.6. The pH for this determination is chosen to be toward the upper end of the pH values of a variety of aqueous latex paints. Thus, a dispersant having a zinc ammonia complex salt which is soluble in the aqueous medium under these conditions will not have a tendency to precipitate or induce the precipitation or flocculation of other paint ingredients. This property permits a pigment paste employing the dispersant of this invention to be used in a wide variety of aqueous latex paint formulations. Zinc in this instance is typical of the multivalent metal ions which may be added as soluble salts or may be produced when reactive pigments are formulated in paints containing high levels of ammonia or amines. Many of the polymer dispersants of the prior art exhibit limited solubility under these conditions and, thus, cannot be used in this pH region and with the pigments which will result in insoluble salts of the dispersant. Examples of such prior art dispersants are given below where it is seen that

storage of 250 hours at a moderately elevated temperature produces marked increase in viscosity of a paint formulated with these prior art materials. It is one of the advantages of the dispersant polymer of this invention that the marked increase in viscosity, on long term storage or on shorter term storage at elevated temperatures, is not observed.

The zinc-ammonia complex test is conducted as follows:

A standard zinc ion solution is made by dissolving 109.7 g of  $Zn(OAc)_2 \cdot 2H_2O$  (0.5 moles) in water, add 148 ml of concentrated ammonia (2.0 moles) and dilute to 1 liter. The pH of this solution is about 9.6 and the solution is a standard 0.5M  $Zn(NH_3)_4^{++}$  solution. Prepare 50 ml of a 0.1N (5meq) solution of the polymer and adjust the pH of this solution to 9.5 using 5 molar hydrochloric acid or sodium hydroxide as needed. Add 1.0 ml of concentrated ammonia to the dispersant polymer solution, then titrate with the standard zinc ammonia complex solution, observing the amount of titrant needed to form a precipitate. If no precipitate is formed when 10 milliliters of the zinc ammonia solution is added, the determination is considered completed and the report of > 10 milliliters indicates that the zinc ammonia complex salt of the polymer is soluble on a 1:1 molar basis. This result indicates that a paint formulated with this dispersant will not be destabilized by the dispersant.

The dispersant copolymers are usually prepared by solution polymerization techniques, preferably in water-miscible media, but bulk, emulsion or non-aqueous dispersion polymerization methods may be desired in special cases. In the usual solution polymerization, the appropriate monomeric mixture is reacted, under oxy-

gen-free conditions, at temperatures in the range of about 30° to 150° C. and in the presence of such free radical initiators as t-butyl peroxypivalate, t-butyl peracetate, ammonium persulfate, t-butyl hydroperoxide, cumene hydroperoxide, and like free radical catalysts including free radical redox polymerization initiators. Catalyst concentrations of about 1 to 15% by weight of the monomers are useful to obtain the low molecular weight polymers desired. Sufficient alkali metal hydroxide, ammonium hydroxide, or water-soluble amine, preferably a slight excess, may be added during polymerization or subsequently to neutralize free acid groups on the copolymer, thus converting the dispersant to the operable salt. The post-polymerization neutralization is preferred. As is well known, catalyst fragments such as derived from a persulfate may appear as part of the polymer. Other known methods of producing low molecular weight polymers may be utilized in place of or in addition to the use of a high proportion of a free radical catalyst. Examples of such other methods are the use of a high polymerization temperature, the use of a chain transfer agent, and all of these together. Among the chain transfer agents are carbon tetrabromide, allyl chloride, thio- $\beta$ -naphthol, thiophenol, butylmercaptan, ethylthioglycolate, mercaptoethanol, isopropylmercaptan, and t-butylmercaptan.

Another method of preparing the copolymer of this invention is by anionic polymerization. A preferred method of anionic polymerization is carried out in the presence of an alkoxide anion which serves as an initiator and an alcohol which serves as a chain regulating agent, as taught by U.S. patent application Ser. No. 517,337, now U.S. Pat. No. 4,103,093 filed Oct. 23, 1974, herein incorporated by reference.

In addition to the dispersant copolymer, an aspect of the invention is the provision of dispersions of pigments as fluid pastes of high solids content and low aqueous medium content (said aqueous medium comprising water or water and a minor or major proportion of alkylene glycol or other water-miscible solvent) containing in admixture a relatively minor amount of the described water-soluble salt of the copolymer of ethylenically unsaturated acid as dispersant. An effective amount of the salt of the copolymer effecting dispersion of solids and fluidity of the pigment paste is employed and will usually not be over about ten percent of the weight of pigment and may be as low as about 0.01%. 0.5% to 7% is preferred and 1% to 5% is most preferred. Many pigment paste and paint recipes of the prior art are greatly improved by the substitution of above 2%, roughly 2% to 4% of the dispersant of this invention for the dispersant of the recipe.

For the preparation of these pigment pastes, it is generally most convenient to prepare an aqueous solution of dispersant copolymer in a salt form. Concentrations of 5 to 40% may be used, although those of 10 to 20% are usually preferred. Pigment, water or other solvent system and solutions are mixed. If desired, the paste or suspension may be ground in a mill—a pebble mill, roll mill, colloid mill, or high speed stone mill, or in some instances a high shear mixer being suitable. Sufficient copolymer is used as the sole dispersant or in admixture with other dispersants to ensure good dispersion and fluidity of the paste. The optimum amount of copolymer will depend upon the specific pigment or pigments and upon the state of subdivision thereof. In general, the finer the particle size the more dispersant should be used. Concentrated pastes can be extended to

give dilute pastes, when the latter are needed. The pigment pastes are a suitable and convenient compositions for addition to aqueous resin latexes or dispersions to form emulsion paints. Moreover, fluid pastes of certain pigments have diverse uses, for example, such high solids content slurries of calcium hydroxide are useful for coatings as white-wash, field markings, or the like, or as concentrated alkaline reagents in chemical manufacturing; dispersions of carbon blacks or other pigments in aqueous media are useful in the fields of paper, cement, water-base paints, coating compositions, inks, rayons, and rubber. The pigments may be present in the foregoing pastes in an amount up to about 85% by weight of the paste.

The pigment pastes of this invention are concentrated dispersions of pigment in water, aqueous solution or water-miscible solvent. They may also contain small amounts of a water soluble binder or a binder latex. In addition to pigments, the paste may contain a dye as an added colorant. The pastes are used in the factory production of paints and as colorant additives to produce custom colors in the paint store or by the painter at the painting site. Several types of paste are used. Factory ground pastes such as the titanium dioxide based pastes used in the examples below are milled at the factory. Other pastes, such as titanium dioxide or clay, may be in the form of a slurry and delivered by tankcar. Others are aqueous colorants for use with latex paints only and generally added to custom-colored paints at the store or by the painter. A variant of these are the universal colorants which may be added to either aqueous latex paints or to oil-based paints. A common practice is to add the colorants to a special paint, called a tint base, adapted for use with colorants.

Many important properties of a paint are in large measure due to the nature of the pigment paste used in formulating the paint. Among these properties are alkaline resistance, exterior durability, low toxicity and low cost for the desired level of performance. Reactive pigments are comparatively little used in latex paints because of the difficulties in obtaining long term storage stability in the presence of polyvalent metal ions. Instability on storage often shows up as an increase in viscosity of the paint sometimes to the point of gelation. One reactive pigment, zinc oxide, is also used as a secondary mildewcide as had lead containing pigments in by-gone days. Other paint properties which are influenced by the nature of the pigment, the dispersant or the grinding medium are flow, leveling, gloss, stain removal, burnish resistance, durability, chalking rate, tint retention, 45 frothing, hiding and so forth. These properties depend on the nature of the extender pigments as well as on the prime pigments and the dispersant.

Concentration of the pigment in a paint is conventionally related to the concentration of binder, both on a volume basis. Pigment volume concentration (PVC) is the ratio of volume of pigment to the volume of total non-volatile materials (pigment and binder) in a coating. Many latex paint properties have been shown to be critically dependent on the PVC. Scrub resistance of a paint decreases with PVC, as does stain removal, however, hiding improves with higher PVC. The critical pigment volume concentration (CPVC) is the level of pigment in the dry paint having just sufficient binder to fill the voids between the pigment particles. Different types of paints differ in the desirable PVC or CPVC values. For instance, ceiling paints are not required to be very washable and can be formulated at or above the

CPVC whereas exterior formulations, particularly gloss paints, are generally formulated well below the CPVC.

In milling or grinding the paste glycols are often used to replace part or all of the water used as the grinding medium. The glycols lower the evaporation rate of the water and thus reduce drying during the grinding. The glycols also contribute anti-freeze and wet edge properties to the paint, the former aiding in shipping and storage of the paint and the latter the brushing properties of the paint, particularly in the region of the lap or overlap of brushed portions. Wet edge time or open time is the length of time a coat of paint remains wet enough to allow "brushing in" at the laps. The amount of grinding medium used varies a great deal and is based on the final one hundred gallons of paint; typical values range from about 50 about 150 pounds.

The dispersant of the present invention protects against flocculation of the pigment, aids the tint retention and hiding of the paint, helps fluidize the pigment slurry for ease of milling or grinding and aids in the color acceptance of colorants in the paste and paint made therefrom for a very wide range of paint formulations. The use formulations include latex paints of the following types: interior and exterior flat, sheen and gloss; corrosion resistant topcoats and primers; wood and alkaline surface topcoats and primers; and so forth. Pigments for the paint industry are normally supplied in fine particle sizes necessary for use in thin coating films. For use in paints these particles must be thoroughly wetted and any pigment conglomerate formed during manufacturing, shipping or storage must be broken up in a high speed disperser, sand mill or other dispersing equipment. Once a good pigment dispersion is produced in forming the pigment paste, the dispersion must be maintained in this condition if the paint formulated therefrom is to perform satisfactorily. It is commonly hypothesized that the dispersant plays a role in both aiding in the breakup of agglomerates and in stabilizing the pigment in the dispersed form. Although this invention is not bound by or related to any specific theory or mechanism of dispersant activity, the following comments are offered as an aid in teaching the invention. Although there are many uncertainties in the theory of the operation of dispersants, it is believed that the dispersant provides a layer which physically prevents contact between different pigment particles and which, by its ionization, furnishes an electrically charged envelope surrounding each pigment particle which acts to repel the like charged neighbor particles. Thus the dispersant prevents particle contact and indeed prevents the particles from getting so close together that surface attractive forces between the particles become strong enough to lead to flocculation of the particles.

In the case of many dispersants, it is important that a minimum amount be employed in the formation of the pigment paste and of the paint. Excess dispersant results in unstable dispersions and flocculation of the pigment in the paste or paint. This is believed, by some experts, to be due to the increased ionic content of the aqueous medium and the so-called double layer effect produces a decrease in the particle separation and thus stability of the dispersion. An important feature of the dispersant of the present invention is that it may be used at high concentrations, in types of paint formulations requiring such high concentrations, without leading to flocculation of the dispersant or sensitivity of the applied coating to water or aqueous solutions. Such sensitivity is markedly reduced or absent in coatings in which the

dispersant of the present invention is employed compared to prior art dispersants. The dispersants of the instant invention are advantageous in paints containing added inorganic or organic salts because of the great stability imparted by these dispersants.

A pigment paste often contains low concentration of other components, other than the pigment, the medium and the dispersant, to achieve specific effects. Wetting agents or surfactants are often used to aid in the dispersion of the pigment. The commonly used ones are anionic surfactants, such as the alkali metal, amine or ammonium salts of alkyl, aryl, alkaryl, aralkyl sulfates, sulfonates, phosphates or phosphonates, or nonionic surfactants such as ethoxylated fatty acids, esters, alcohols, amines, amides, phenols or the corresponding sulfur-containing compounds. The anionic surfactants may also comprise ether or polyether units and the nonionic surfactants may also comprise alkoxyl units other than ethoxyl, such as propoxyl. In general, high foaming surfactants are avoided because the use of such surfactants would lead to excess foam during the milling or grinding of the paste or require a high level of defoamer to be added to the paste formulation. High levels of defoamer are to be avoided, however, because these often lead to color acceptance problems. In general the surfactants aid in obtaining full color development from the pigment. Common use levels for the defoamer are 1 to 4 pounds per 100 gallons of the final paint formulation. Although there is great variability in formulating for different types of paint, a rough rule of thumb is to add half of the defoamer in the pigment paste and the other half in the let down when manufacturing the paint from the pigment paste. Thickeners are used to increase the viscosity or modify the flow or rheology of the paint made from the pigment paste. Examples of the rheology modification desired are:

1. To increase drag for improved film build;
2. To impart thixotropy for improved pigment suspension stability;
3. To reduce dripping from the brush or roller;
4. To reduce spattering during the roller application (poorly selected thickeners can cause increased spattering).

Among the typical thickeners are hydroxyethyl cellulose, polyacrylic acid, and Attapulgite clay. These are generally used as 2 to 4% aqueous solutions when added to the pigment paste mix or to the paint.

In testing dispersant polymers, to determine their suitability for a wide range of paint formulations, corrosion resistant paint formulations are very useful for screening purposes. A paint formulated with reactive pigment such as zinc oxide and lead silicochromate offer problems to the paint formulator. One particular problem is that at high pH in the presence of ammonia, some of the zinc oxide dissolves to furnish multivalent cations. These multivalent cations can act as precipitants for dispersant polymers. Any dispersant precipitated, of course, is no longer active as a dispersant and indeed the precipitated gel may serve as a focal point for agglomeration of pigment or binder latex in a formulated paint. Thus viscosity stability determinations on aged and heat aged paints are sensitive measures of the suitability of a dispersant insofar as its capability of imparting stability to the paint is concerned. When the corrosion resistant paint is applied to a ferrous surface and tested for the corrosion resistance imparted to the surface, the paint undergoes one of the most searching tests available. Only a tough, well integrated, pore-free,

impervious coating will pass the battery of corrosion resistance tests. Any dispersant polymer which detracts from these properties is, of course, also unsuited for use in some of the other paint formulations. A dispersant which performs well in a model corrosion-resistant paint formulation will also perform well in a wide range of paint formulations.

The following examples further illustrate the invention, but are not intended to limit it in any way the invention being defined only by the claims. Unless otherwise noted, all parts are by weight and all temperatures are in degrees Centigrade. The first group of examples hereinbelow teach the polymerization processes and compositions of dispersant polymers. The later examples teach the preparation of pigment pastes and of paints made therefrom and the testing of these paints when used as coatings, thereby illustrating particular unique features of the dispersant polymers of this invention. Abbreviations used in the examples include BMA for n-butyl methacrylate, MAA for methacrylic acid, MMA for methyl methacrylate, LMA for lauryl methacrylate, PG for propylene glycol, Mn for number average molecular weight and Mw for weight average molecular weight.

#### EXAMPLES 1-3

##### AMMONIUM SALTS OF BMA/MAA COPOLYMERS VIA FREE RADICAL INITIATION

To prepare the polymer of Example 1 (BMA/MAA = 62/38 by weight), a 2-liter, four-necked, round bottomed flask equipped with a mechanical stirrer, a nitrogen ebulliator, a thermometer, a condenser, two Claisen adapters, two addition funnels, and a heating mantle atop a thermosensor controlled pot-lifter is charged with 430 g of isopropanol. Dry nitrogen ebullition is begun and the solvent heated to reflux. A monomer mixture made up of 177.5 g (1.25 mole) of BMA and 107.5 g (1.25 mole) of MAA is charged over one hour; simultaneously, an initiation solution made up of 17.07 g of 75% t-butylperoxypivalate in mineral spirits in 100 g of isopropanol is charged. The reaction mixture gradually thickens. After completion of the additions, the mixture is maintained at reflux for an additional hour and then cooled.

A portion (300 g) of the polymer is charged to a 1-liter, four-necked, round bottomed flask fitted with a mechanical stirrer, a nitrogen inlet, a distillation head atop a foam trap, a thermometer, a heating mantle atop a controlled pot-lifter, two addition funnels and two Claisen adapters. The pot contents are heated until distillation begins. Water and 28% aqueous ammonium hydroxide are charged to separate addition funnels. Water is added and a distillate made up of the water-isopropanol azeotrope is obtained (some ammonia is also lost during this solvent exchange); aqueous ammonium hydroxide solution being added at a rate such that homogeneity is maintained. Water addition and distillation are continued until the distillate temperature reaches 100° C. indicating depletion of isopropanol from the product. The solution is cooled and the pH is adjusted to 9.7 by addition of more aqueous ammonium hydroxide. Solids (150° C./1 hr.) are measured then adjusted to 25% by addition of water. Brookfield viscosity (Brookfield Synchro-Lectric Viscometer LVI) is 3600 cps and the pKa is 7.0. Mn is 5,000 and Mw is 14,000 for the acid form of the polymer.

Example 2 is prepared by the procedure of Example 1 but changing the weight ratios to 30% BMA, 70% MAA. For Example 3, the weight ratios are 77% BMA, 23% MAA.

#### EXAMPLES 4 and 5

#### POLYMERS PREPARED BY SAPONIFICATION OF ANIONICALLY INITIATED POLYMERIZATIONS

To prepare the polymer of Example 4, BMA/MAA about 70/30 by weight, the procedure of Example 1, Method C of U.S. patent application, now U.S. Pat. No. 4,103,093 Ser. No. 517,337, filed on Oct. 23, 1974 for "Novel Methacrylic Polymers Having Condensation Crosslinkable Functionality", herein incorporated by reference, is used. The procedure, as given on pages 32-34 of said application, is employed with n-butyl methacrylate in place of the methyl methacrylate used in the referenced Example 1. The reaction temperature is 80° C., the conversion is 99% after four hours of 20 reaction using about 1.0 to 1.5 mole percent of potassium methoxide catalyst and 15 mole percent n-butanol, based on the n-butyl methacrylate. The product has a weight average molecular weight about 1,000 with more than 90% by weight being between 350 and 2,200 in molecular weight. The polymer, at about 85-90% solids in toluene, is treated with 50 equivalents percent (based on total ester equivalents) of potassium hydroxide (50%) at 60° C. The heterogeneous mixture is stirred at full reflux (85°-105° C.) for 1-2 hours until exotherm 30 is established and the pellets dissolve and react. After two additional hours at reflux, conversion to carboxylate reaches 94% of potassium hydroxide (about 3.0-3.3) carboxylate functionality. The crude potassium salt is treated with 105 equivalent-% of concentrated sulfuric acid at 45° to 65° C. and a suitable solvent to retain 35 solubility of the organic acid (ketones, ester solvents, etc.). The sulfate salt is removed by centrifugation or repeated water washes. The organic layer is vacuum azeotropically dried at 70° to 80° C. and filtered free of 40 residual insoluble inorganic sulfate salts, providing a clear, pale-yellow-liquid of 35,000 cps viscosity at 70% solids in toluene/n-butanol/25° C. Acid number (100% solids) is 200.

The polymer of Example 5 is the polymer of Example 4 converted to the ammonium salt by dilution to ca. 20% solids by a mixture of 7 parts water, 2 parts toluene and 1 part isobutanol. Sulfuric acid (97%) is added carefully over a 15 minute period, with cooling, until about 10% excess over the charged caustic is present. The white, mobile, two phase mixture is agitated for 15-20 minutes, the aqueous layer removed and replaced by an equal amount of fresh water. The mixture is heated to 60°-70° C. under vacuum, the toluene removed as distillate, the pressure raised to one atmosphere and the temperature to 100° C. until the total distillate is about 1/2 greater than the charged toluene and isobutanol. The temperature is allowed to fall to 90° C. and aqua ammonia is added until the white, two phase soft gum is dissolved. The solution is cooled to 60°-65° C. and about half as much ammonia is added bringing the pH to about 9.5.

#### EXAMPLES 6-14

#### OTHER FREE RADICAL INITIATED ACRYLIC COPOLYMER

In these examples, the procedure of Example 1 is used to make the polymer. The polymers are then converted

to the sodium salt form, rather than the ammonium salt form as in Example 1, by utilizing 50% aqueous sodium hydroxide in place of the 28% aqueous ammonium hydroxide recited in Example 1. The compositions are

5 (by weight percent):

Example 6: MMA/MAA = 46/54

Example 7: MMA/MAA = 62/38

Example 8: MMA/MAA = 70/30

Example 9: BMA/MAA = 40/60

10 Example 10: BMA/MAA = 50/50

Example 11: BMA/MAA = 55/45

Example 12: BMA/MAA = 65/35

Example 13: LMA/MAA = 62/38

15 Example 14: LMA/MAA = 35/65

#### EXAMPLE 15

#### FREE RADICAL INITIATED STYRENE-METHACRYLIC ACID COPOLYMER

The sodium salt of a 45% styrene, 55% methacrylic acid copolymer is prepared as follows:

Reagents:	Propylene glycol (PG)	300.0	g	
	Styrene	135.0	g	(1.30 moles)
	Methacrylic acid	165.0	g	(1.92 moles)
	Mercaptoethanol	3.0	g	
	70% t-Butyl peracetate	9.0	g	
	in mineral spirits	0.9	g	

A 1-liter, four-necked, round bottomed flask equipped with a mechanical stirrer, two addition funnels, a distillation head with a variable takeoff, a thermometer, a nitrogen inlet, and a heating mantle atop a thermosensor-controlled pot lifter is charged with 300 g of propylene glycol. This heel charge is heated to 150° C. under nitrogen. The monomer charge (135 g styrene, 165 g methacrylic acid, and 3 g mercaptoethanol) is gradually charged over 5 hours. Simultaneously, the initiator solution (9.0 g of 70% t-butyl peracetate) is added over the same period. After completion of the feeds, an additional 0.9 g of t-butyl peracetate solution is added and the batch held at 150° C. for another hour.

Vacuum (finally to 25 mm) is applied to distill 130 g of propylene glycol containing unreacted methacrylic acid and styrene.

The copolymer solution is cooled and neutralized with 286 g of 25% aqueous sodium hydroxide solution to give a final product pH of 10.1; theoretical solids = 49.1%, theoretical PG content = 22.5%, viscosity 7650 cps.

#### EXAMPLE 16

#### FREE RADICAL BMA/MAA COPOLYMER

The sodium salt of BMA/MAA = 62/38, by weight, is prepared by a modification of the procedure of Example 15. Using the same equipment, the polymerization is carried out with the following materials.

Materials	Grams/1,000 grams product
1. Propylene glycol	261.3
2. n-butyl methacrylate	237.8
3. Methacrylic acid	145.8
4. Mercaptoethanol	3.8
5. t-butyl hydroperoxide (70% aqueous)	17.0
6. t-butyl hydroperoxide (70% aqueous)-chaser	1.7
7. Ammonium hydroxide (aqua ammonia)	102.9

-continued

Materials	Grams/1,000 grams product
8. Water	229.8 grams*

\*plus the weight of the distillate removed during the polymerization.

A nitrogen blanket and a temperature of 150° C. is maintained throughout the polymerization. The flask is charged with 90% of the propylene glycol and is heated to 150° C. Materials 2, 3 and 4 are mixed and fed concurrently with a mixture of 5 and the remainder of 1 over a period of five hours. Toward the end of the polymerization, some distillate is removed to maintain the 150° C. pot temperature. Upon completion of the feed, the flask is held at 150° C. for a period of 15 to 30 minutes then the chaser, material 6, is added. Following a one-hour hold at 150° C., the product is cooled to 75° to 80° C. and materials 7 and 8 are added. The final product is a slightly hazy, yellowish liquid at about 40% solids in a propylene glycol/water solution (approximately 40% propylene glycol). The viscosity is about 4,200 centipoises measured at 25° C. and the pH about 9.5. The number average molecular weight is 2,470 and the weight average molecular weight is 6,670, for the polymer in the acid form; number average molecular weight being determined by vapor phase osmometry and weight average calculated from the number average and the polydispersity, 2.7, estimated from the molecular weight distribution determined via gel permeation chromatography.

In an alternative process, material 4, the mercaptoethanol, is mixed with the propylene glycol in the kettle charge rather than with the monomers of the continuous feed. The product made this way has the same appearance and solids. Its viscosity is 3,700 centipoises at 25° C. and pH 9.8.

## EXAMPLE 17

## PRIOR ART DISPERSANTS

- (A) Sodium salt of p-MAA (Mn ca. 4000-5000), 30% solids
- (B) Sodium salt of diisobutylene/maleic anhydride copolymer, 25% solids
- (C) Ammonium salt of half amide of diisobutylene/maleic anhydride (21%)
- (D) Sodium salt of acrylic copolymer comprising carboxylate mers. 40% solids, Dispex G-40, Allied Colloids
- (E) Sodium salt of polycarboxylic acid, 25% solids, Colloid III, Colloids Inc.
- (F) Ammonium salt of polycarboxylic acid, 25% solids, Colloids IIM, Colloids Inc.
- (G) Organic Phosphate, 90% solids, Strodex PK-90, Dexter Chemical
- (H) Ammonium salt of styrene/maleic ester copolymer, 35% solids SMA 144OH (Arco Chemical)
- (I) Ammonium salt of p-MAA, Example 17A above, 25% solids

## EXAMPLE 18

CORROSION INHIBITING PAINTS UTILIZING  
PRIOR ART DISPERSANTS

The following are charged to a suitable vessel (steel beaker) and ground in a high speed dispersing mill, here

a Cowles dissolver at about 4,000 feet per minute for 15 minutes, to give a pigment paste having 0.56% dispersant on pigment, by weight:

Grind	Pounds/100 gal.
Water	60.0
Dispersant (solids basis)	2.5
Water	6.4
10 Octyl phenyl poly(16)oxyethylene	
benzyl ether (wetting agent)	2.2
Nopco NXZ (Nopco) (antifoamer)	2.2
Ethylene glycol	22.0
Hydroxyethyl cellulose,	
Natrosol 250 MR (Hercules)	
24% (thickener)	65.6
Rutile titanium dioxide,	
TiPure R-966 (DuPont)	209.4
325 mesh water-ground mica (English Mica)	
Whiting, calcium carbonate,	
Suspensol (Diamond Alkali)	125.0
Zinc oxide, Kador 15	6.0
Basic lead silico chromate,	
Oncor M-50 (National Lead)	80.0

The above is then let down at a lower speed with the following:

Letdown	Pounds/100 gal.
Ammonium carbonate	15.0
An acrylic latex at about 46% solids containing about 1% ethyl acrylate, about 1% methyl acrylate, about 2% of a polar-group-containing monomer as described in U.S. Pat. No. 3,356,627 and the remainder methyl methacrylate	pre-mix
2,2,4-trimethylpentanediol-1,3-monoisobutyrate	5.0
2-n-octyl-4'-isothiazolin-3-one, 45% active (mildewcide)	pre-mix
Nopco NXZ (Nopco) (antifoamer)	2.0
	2.2

The pH is adjusted to 9.6 using aqua ammonia.

After equilibration at room temperature for seven days, the paints are brush applied to clean cold rolled steel to yield a 2 mil dry film thickness in two coats. The second coat is applied 18 hours after the first. The panels are allowed to dry one week at ambient conditions and then subjected to salt spray and water fog corrosion resistance tests for 500 hours (ASTM-B-117 and D-1735). Performance is rated in terms of degree of undercoat rusting and blistering of the coating (ASTM D-772). Both low shear Stormer viscosity and high shear ICI brushing viscosity of the paints are measured initially, and after 250 hours storage at room temperature and at 140° F. The Stormer viscosity is reported in Krebs Unit and is measured by the method of ASTM D562-55 (reapproved 1972). The ICI viscosity is reported in poise and is measured by the ICI cone and plate viscometer of Research Equipment (London) Ltd.

Paint Dispersant	18A Ex.17A	18B Ex.17B	18C Ex.17D	18D Ex.17H	18E Ex.17C	18F Ex.17G	18G Ex.17E	18H Ex.17F
Dispersant Level (lb/100 gal)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Dispersant pKa	5.9	4.0/9.8	4.8	6.5	6.5	—	—	—
Zinc ammonia complex test	>10.0	5.5	>10.0	<1.5	>10.0	—	—	—
<u>Stormer Viscosity (Krebs Units)</u>								
initial	70	68	70	70	70	74	72	72
250 hours at 77° F. (unsheared)	82	77	81	81	88	76	76	76
(sheared)	78	76	78	78	83	74	76	76
250 hours at 140° F. (unsheared)	89	104	95	100	108	104	104	122
(sheared)	82	85	82	88	85	89	89	89
<u>High Shear Viscosity (ICI poise)</u>								
250 hours at 77° F.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4
250 hours at 140° F.	0.7	0.9	0.5	1.0	1.0	0.9	1.0	1.1
<u>Corrosion Resistance</u>								
500 hours salt spray								
undercoat rusting	moderate	none	slight	none	none	none	none	none
blister (size)	7	—	8	—	—	—	—	—
blister (density)	dense	none	sight	none	none	none	none	none
500 hours high humidity								
undercoat rusting	slight	none	heavy	sl-med	slight	trace	slight	moderate
blister (size)	7	—	7	7	9	9	8	8
blister (density)	medium	none	sl-med	sl-med	slight	trace	slight	moderate

The performance of the prior art dispersants as indicated by the data in Table 11, can be separated into two

17I and 2) exhibit greater corrosion than the others as indicated by the salt spray test.

Paint Dispersant	19A Ex. 17B	19B Ex. 17A	19C Ex. 17I	19D Ex. 9	19E Ex. 2	19F Ex. 10	19G Ex. 1	19H Ex. 3
Dispersant Level (lb/100 gal)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Dispersant pKa	4.0/9.8	5.9	5.9	6.5	6.1	6.4	7.0	7.3
Zinc ammonia complex test	5.5	>10.0	>10.0	>10.0	>10.0	>10.0	>10.0	<1.5
<u>Stormer Viscosity (Krebs Units)</u>								
initial	72	72	72	72	72	72	72	74
250 hours at 77° F. (unsheared)	77	77	79	78	77	78	83	95
(sheared)	74	77	77	76	77	74	77	86
250 hours at 140° F. (unsheared)	122	89	85	85	82	100	100	>140
(sheared)	97	82	79	78	73	82	80	98
<u>High Shear Viscosity (ICI poise)</u>								
250 hours at 77° F.	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.7
140° F.	1.2	0.3	0.6	0.5	0.5	0.6	0.7	1.3
<u>Corrosion Resistance</u>								
500 hours salt spray								
undercoat rusting	none	med.dense	dense	med.	med.dense	trace	trace	none
blister (size)	—	7	8	7	8	—	—	—
blister (density)	none	med.dense	dense	med.	med.dense	trace	none	trace
500 hours high humidity								
undercoat rusting	med.dense	slight	slight	none	med.dense	slight	slight	med.
blister (size)	8	7	7	9	8	8	8	9
blister (density)	med.dense	slight	slight	slight	med.dense	slight	med.dense	med.

categories.

(1) Dispersants with good maintenance (500 hour salt spray) but poor viscosity stability (particularly unsheared heat-aged vs. unsheared room temperature aged Stormer viscosity and high shear viscosity) as exemplified by paints in the Example 18 series (BDEFGH).

(2) Other dispersants had poor maintenance (corrosion resistance) properties but acceptable viscosity stability; these are exemplified by paints 18A and 18C.

#### EXAMPLE 19

#### PAINTS PREPARED WITH THE DISPERSANTS OF EXAMPLES 1, 2, 3, 9, 10 AND THE PRIOR ART

The paints were prepared and evaluated by the methods given in Example 18. The results are in the following table. Examples 19A and 19H (dispersants of examples 17B and 3) have limited storage stability as evidenced by the increasing viscosity of the paint stored, particularly stored at an elevated temperature. Examples 19B, 19C and 19E (dispersants of examples 17A,

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#### EXAMPLE 20

#### DRYING OIL MODIFIED CORROSION INHIBITING PAINTS USING THE DISPERSANTS OF EXAMPLES 4 and 5

Drying oils are frequently added to latex maintenance paints for increased protection of ferrous surfaces that have already rusted. It is especially difficult to achieve paint stability in this type of system so the effectiveness of the dispersant is particularly important.

Oil modified latex paints having the following ingredients are prepared and evaluated, according to the procedures described in Example 18, using the following formulation.

Grind	Pounds/100 gal.
Water	44.4
Dispersant (dry basis)	variable, indicated in the table below

-continued

Grind	Pounds/100 gal.
Octyl phenyl poly(16)oxyethylene benzyl ether (wetting agent)	2.2
Nopco NXZ (Nopco) (antifoamer)	2.2
Ethylene glycol	22.0
Hydroxyethyl cellulose, Natrosol 250 MR (Hercules) (2 1/2 %) (thickener)	65.6
Rutile titanium dioxide, TiPure R-966 (duPont)	209.4
325 mesh water-ground mica (English Mica)	26.0
Whiting, calcium carbonate, Suspenso (Diamond Alkali)	125.0
Zinc oxide, Kadox 15	6.0
Basic lead silico chromate, Oncor M-50 (National Lead)	80.0
Ammonium carbonate	12.0
An acrylic latex at about 46% solids containing about 3 ethyl acrylate, 3 methyl methacrylate and about 1% methacrylic acid	480.0

pre-  
mix

-continued

Grind	Pounds/100 gal.
Water	29.30
Hydroxyethyl cellulose, Natrosol 250 MR (Hercules) (2 1/2 %) (thickener)	29.30

5 The pH is adjusted to 9.6 with ammonia.

10 The results of the heat stability and corrosion resistance tests are given in the following table. Even at low use levels, the conventional polyacrylate dispersant has poor salt spray resistance (Paint 20A). At the same low use level, the olefin/maleic anhydride dispersant confers excellent corrosion resistance but stability is unacceptable (Paint 20B). At higher use levels stability is somewhat improved but corrosion resistance is sacrificed (Paint 20C). On the other hand, comparably high levels of the dispersants of Examples 4 and 5 not only confer excellent stability, but corrosion resistance is also preserved (Paints 20D and 20E).

15

20

Paint Dispersant	20A Ex.17A	20B Ex.17B	20C Ex.17B	20D Ex.4	20E Ex.5
Dispersant Level (lb/100 gal)	2.5	2.5	10.0	10.0	10.0
Dispersant pKa	5.9	4.0,9.8	4.0,9.8	6.9	6.9
Zinc ammonia complex test	>10.0	5.5	5.5	>10.0	>10.0
<b>Stormer Viscosity (Krebs Units)</b>					
initial	72	72	72	77	77
250 hours at 77° F. (unsheared)	82	77	80	82	77
(sheared)	77	75	77	77	77
250 hours at 140° F. (unsheared)	86	104	95	89	89
(sheared)	82	89	86	82	82
<b>High Shear Viscosity</b>					
250 hours at 77° F.	0.6	0.5	0.6	0.6	0.6
250 hours at 140° F.	0.7	1.4	0.6	0.6	0.6
<b>Corrosion Resistance</b>					
500 hours salt spray					
undercoat rusting	medium	none	medium	none	none
blister (size)	8	—	8	—	—
blister (density)	medium	none	medium	none	none
500 hours high humidity					
undercoat rusting	slight	slight	medium	trace	sl-med
blister (size)	9	7	4	7	7
blister (density)	slight	slight	medium	med.dense	sl-med

Tung Oil	44.2
Octyl phenyl poly(8.7)ethoxy- ethanol	3.14
Octyl phenyl poly(39)ethoxy- ethanol	1.73
2,2,4-trimethylpentanediol -1,3-monoisobutyrate	4.0
Nopco NXZ (Nopco) (antifoamer)	2.0
2-n-octyl-4'-isothiazolin-3- one 45% active	2.0
6% Co Naphthenate	0.21
6% Zr Octoate	3.52

pre-  
mix

### EXAMPLE 21

PAINTS FORMULATED WITH THE  
DISPERSANTS OF EXAMPLES 11, 12 AND  
THOSE OF THE PRIOR ART

50 Paints are prepared and evaluated using the procedures of Example 18 except that the amount of zinc oxide in the formulation is increased to 9 pounds per 100 gallons from the usual 6 pounds per 100 gallons. At the higher zinc oxide levels, it is seen that the paints are more unstable when the prior art dispersants are used than when the dispersants of this invention are used.

Paint Dispersant	21A Ex.17B	21B Ex.17A	21C Ex.11	21D Ex.12
Dispersant Level (lb/100 gal)	5.0	2.5	5.0	5.0
Dispersant pKa	4.0,9.8	5.9	6.4	6.8
Zinc ammonia complex test	5.5	>10.0	>10.0	>10.0
<b>Stormer Viscosity (Krebs Units)</b>				
initial	72	72	72	72
250 hours at 77° F. (unsheared)	77	82	77	74
(sheared)	72	79	75	74
250 hours at 140° F. (unsheared)	138	95	89	89
(sheared)	95	86	80	80

-continued

Paint Dispersant	21A Ex.17B	21B Ex.17A	21C Ex.11	21D Ex.12
<u>High Shear Viscosity (ICI poise)</u>				
250 hours at 77° F.	0.5	0.5	0.5	0.5
140° F.	1.2	1.0	0.7	0.7
<u>Corrosion Resistance</u>				
500 hours salt spray				
undercoat rusting	light	mod-dense	mod-dense	moderate
blister (size)	8	6	7	8
blister (density)	light	mod-dense	mod-dense	moderate
500 hours high humidity				
undercoat rusting	none	slight	trace	slight
blister (size)	—	7	9	9
blister (density)	none	slight	trace	slight

## EXAMPLE 22

## PAINTS FORMULATED WITH THE DISPERSANTS OF EXAMPLES 6, 7, 8 AND THOSE OF THE PRIOR ART

Paints are prepared and evaluated using the procedures of Example 18. The results are given in the following table. The viscosity stability and maintenance properties are to be carefully compared to the dispersant pKa and the solubilities of the zinc complex.

-continued

Paint Dispersant	23A Ex.17A	23B Ex.17B	23C Ex.15	23D Ex.16
(unsheared)	81	80	76	78
(sheared)	76	78	74	76
250 hours at 140° F.				
(unsheared)	85	>141	79	85
(sheared)	77	>141	74	77
<u>High Shear Viscosity (poise)</u>				
250 hours at 77° F.	0.5	0.5	0.4	0.4
140° F.	0.5	—	0.4	0.5

Paint Dispersant	22A Ex.17A	22B Ex.17B	22C Ex.6	22D Ex.7	22E Ex.8
Dispersant Level (lb/100 gal)	2.5	2.5	2.5	2.5	2.5
Dispersant pKa	5.9	4.0,9.8	5.9	6.0	6.2
Zinc ammonia complex test	>10.0	5.5	>10.0	>10.0	>10.0
<u>Stormer Viscosity (Krebs Units)</u>					
initial	70	70	76	76	76
250 hours at 77° F. (unsheared)	77	75	82	85	88
(sheared)	74	72	77	82	82
250 hours at 140° F. (unsheared)	77	86	89	93	94
(sheared)	74	77	80	86	86
<u>High Shear Viscosity (ICI poise)</u>					
250 hours at 77° F.	0.4	0.5	0.5	0.5	0.5
140° F.	0.4	0.6	0.5	0.7	0.8
<u>Corrosion Resistance</u>					
500 hours salt spray					
undercoat rusting	med-dense	none	med-dense	med-dense	sl-med
blister (size)	8	—	8	8	8
blister (density)	med-dense	none	med-dense	med-dense	sl-med
500 hours high humidity					
undercoat rusting	trace	slight	slight	none	none
blister (size)	6	9	9	—	—
blister (density)	trace	slight	slight	none	none

## EXAMPLE 23

## DRYING OIL MODIFIED PAINT PREPARED WITH THE DISPERSANTS OF EXAMPLES 15, 16 AND 16 AND THE PRIOR ART

Using the oil modified formulation of Example 20 and the procedures of Example 18, paints were made and evaluated. The results are in the table below. Even at high use level the dispersants of Examples 15 and 16 produced paints of good stability.

50	<u>Corrosion Resistance</u>
<u>500 hours salt spray</u>	
undercoat rusting	moderate
blister (size)	none
blister (density)	none

55	
We claim:	
1.	A pigment paste, adapted for use in a wide variety of aqueous latex paints, comprising a water-compatible suspension of a finely divided pigment and, for dispersion thereof, an effective amount of a water soluble dispersant comprising (1) an addition copolymer of greater than about 30 % by weight of an $\alpha$ ; $\beta$ -unsaturated monovinylidene carboxylic acid or a mixture of such acids and (2) at least one other ethylenically unsaturated monomer, the copolymer having an apparent pKa between 6.0 and 7.5 and a number average molecular weight between about 500 and about 15,000;
60	
2.	
3.	
65	

Paint Dispersant	23A Ex.17A	23B Ex.17B	23C Ex.15	23D Ex.16
Dispersant Level (lb/100 gal)	2.5	2.5	8.3	8.3
Dispersant pKa	5.9	4.0,9.8	7.0	6.9
Zinc ammonia complex test	>10.0	5.5	—	—
<u>Stormer Viscosity (Krebs Units)</u>				
initial	76	76	74	74
250 hours at 77° F.	—	—	—	—

the copolymer being characterized by forming a water soluble salt with a zinc ammonia complex ion at a pH of 9.6.

2. The paste of claim 1 in which the number average molecular weight of the copolymer is between 1,000 and 6,000, the apparent pKa is between 6.3 and 7.2 and the amount of the copolymer is 0.01% to 10% on the weight of the pigment.

3. The paste of claim 2 in which the copolymer is a copolymer of 30 to 70% by weight of the carboxylic acid and at least 30% by weight of a hydrocarbon monomer, a C<sub>1</sub>-C<sub>18</sub> ester of acrylic acid, a C<sub>1</sub>-C<sub>18</sub> ester of methacrylic acid or a mixture thereof.

4. The paste of claim 3 wherein the pKa is between 6.5 and 7.0, the number average molecular weight is between 2,000 and 4,000 and the copolymer is a copolymer of 30 to 50% by weight of acrylic, methacrylic or itaconic acids or a mixture thereof.

5. The paste of claim 4 wherein the copolymer is 0.5% to 7% by weight of the pigment and comprises 50 to 70% by weight of C<sub>1</sub>-C<sub>8</sub> alkyl methacrylate mer units, C<sub>1</sub>-C<sub>8</sub> alkyl acrylate mer units or a mixture thereof and wherein the pigment comprises a multivalent metal compound.

6. The paste of claim 5 wherein the copolymer is 1% to 5% of the weight of the pigment and comprises 35 to 40% by weight methacrylic acid mer units and 60 to 65% by weight of C<sub>2</sub>-C<sub>4</sub> alkyl methacrylate mer units, C<sub>2</sub>-C<sub>4</sub> alkyl acrylate mer units or a mixture thereof and wherein the metal compound is zinc oxide.

7. A process for preparing a pigment paste comprising adding to a vessel paste components comprising (A) water, (B) a pigment, (C) about 0.01% to about 10%, on the weight of the pigment, of a water-soluble dispersant comprising (1) an addition copolymer of greater than about 30% by weight of an  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid or a mixture of such acids and (2) at least one other ethylenically unsaturated monomer, the copolymer having an apparent pKa between 6.0 and 7.5 and a number average molecular weight between about 500 and about 15,000; the copolymer being characterized by forming a water soluble salt with

a zinc ammonia complex ion at a pH 9.6; and, optionally, (D) a wetting agent, an antifoam agent, a solvent, a thickener or any combination thereof and grinding the components under high shear to form a paste.

8. The paste prepared by the process of claim 7.

9. A water-soluble dispersant copolymer, adapted for use in pigment paste, consisting of (1) at least about 30% by weight of an  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid or a mixture of such acids and (2) at least one other ethylenically unsaturated monomer, the copolymer having an apparent pKa between 6.0 and 7.5 and a number average molecular weight between about 500 and about 15,000; the copolymer being characterized by forming a water-soluble salt with a zinc ammonia complex ion at a pH of 9.6.

10. The copolymer of claim 9 in which the number average molecular weight is between 1,000 and 6,000 and the apparent pKa is between 6.3 and 7.2.

11. The copolymer of claim 10 comprising 25 to 70% by weight of  $\alpha,\beta$ -unsaturated monovinylidene carboxylic acid mer units and at least 30% by weight of mer units derived from a hydrocarbon monomer, a C<sub>1</sub>-C<sub>18</sub> ester of acrylic acid, a C<sub>1</sub>-C<sub>18</sub> ester of methacrylic acid or a mixture thereof.

12. The copolymer of claim 11 having a pKa between 6.5 and 7.0, a number average molecular weight between 2,000 and 4,000 and being a copolymer of 30 to 50% by weight of acrylic, methacrylic or itaconic acids or a mixture thereof.

13. The copolymer of claim 12 wherein the copolymer is 0.5% to 7% by weight of the pigment and is a copolymer of 50 to 70% by weight of C<sub>1</sub>-C<sub>8</sub> alkyl methacrylate mer units, C<sub>1</sub>-C<sub>8</sub> alkyl acrylate mer units or a mixture thereof.

14. The copolymer of claim 13 wherein the copolymer is 1% to 5% of the weight of the pigment and comprises 35 to 40% by weight methacrylic acid mer units and 60 to 65% by weight of C<sub>2</sub>-C<sub>4</sub> alkyl methacrylate mer units, C<sub>2</sub>-C<sub>4</sub> alkyl acrylate mer units or a mixture thereof.

\* \* \* \* \*

EXHIBIT  
H

# United States Patent [19]

Kowalski et al.

[11] Patent Number: 4,880,842

[45] Date of Patent: Nov. 14, 1989

[54] MULTI-STAGE OPACIFYING POLYMER PARTICLES CONTAINING NON-POLYMERIC ACID ABSORBED THEREIN

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[73] Assignee: Rohm & Haas Company

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[58] Field of Search 525/301, 902; 521/64, 521/57, 54, 134; 523/201

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4,325,856	4/1982	Ishikawa et al.	523/201
4,419,496	12/1983	Henton et al.	525/301
4,427,836	1/1984	Kowalski et al.	525/301
4,468,498	8/1984	Kowalski et al.	525/301
4,469,825	9/1984	Kowalski et al.	523/201
4,497,917	2/1985	Upsom et al.	523/201
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## ABSTRACT

Multi-stage polymer particles containing one or more void space(s) therein are produced by sequential emulsion polymerization of an essentially low-acid earlier polymer stage, encapsulation of said low-acid polymer stage with at least a final polymer stage, contacting said polymer particles with a non-polymeric carboxylic acid to permit the acid to be absorbed into said low-acid polymer stage and swelling the polymer particles by contacting the particles with an aqueous base. The low-acid polymer stage is formed by emulsion polymerizing a monomer system comprising ethylenically unsaturated monomer(s) and containing less than 5% by weight of monomer(s) containing acid functionality. The low-acid polymer stage is subsequently encapsulated by one or more polymer stages by emulsion polymerizing ethylenically unsaturated monomer(s) in the presence of the low-acid polymer stage. The final stage has a glass transition temperature (Tg) of about 50° C. or greater, and the total polymer stages having a Tg of about 50° C. or greater comprise about 60% or more by weight of the polymer particles. A non-polymeric carboxylic acid is absorbed into the polymer particles and the resultant particles are contacted with base at a pH sufficient to swell the particles with water at a temperature near or above the Tg of the neat polymer or plasticized polymer of the final polymer stage. When dried the particles contain void space(s) therein which produce(s) opacity in compositions in which the particles are contained.

13 Claims, No Drawings

MULTI-STAGE OPACIFYING POLYMER  
PARTICLES CONTAINING NON-POLYMERIC  
ACID ABSORBED THEREIN

BACKGROUND OF THE INVENTION

This invention relates to multi-stage polymer particles containing void space(s) therein which are useful as binding or opacifying agents in coating, impregnating and molding compositions.

Core-shell polymer particles are disclosed in U.S. Pat. No. 4,427,836. The polymer particles of the '836 patent are prepared by sequentially emulsion polymerizing a core monomer system comprising monoethylenically unsaturated monomers, one of which has a carboxylic acid group and said carboxylic acid group containing monomer comprising at least 5% by weight of the core monomer system, polymerizing in the presence of the core polymer dispersion a shell monomer system which is permeable to aqueous volatile base selected from ammonia and amines, and neutralizing with ammonia or amine so as to swell said core and form particles which, when dried, contain a single void and cause opacity in compositions in which they are contained. The '836 patent requires that the carboxylic acid be present in the core in a polymeric form. The composition of the shell polymer is such as to be not permeable to fixed or permanent base according to said patent "so that films deposited from aqueous coating compositions comprising a volatile base-swollen core of the core-sheath polymer upon drying and resultant (at least partial) removal by volatilization of the base are not damaged by any permanent base present in the substrate coated or in solutions used later for cleaning the films." (Column 3, lines 35-45). Said patent teaches that "suitable swelling agents for acid-containing cores are ammonia, ammonium hydroxide, or a volatile lower aliphatic amine, such as trimethylamine, and triethylamine." Similarly, U.S. Pat. No. 4,468,498 discloses core-shell polymers having a core of polymeric acid and being swellable by a volatile base.

U.S. Pat. No. 4,594,363 discloses a process for making core-shell polymer particles similar to the '836 patent, except that a fixed or permanent base is used to swell the particles. The '363 patent also requires that the core be polymerized from at least 5% by weight of acid-functional monomer.

U.S. Pat. No. 4,469,825 discloses core-shell polymers having cores which are swellable by acid. High levels of copolymerized acid in the core polymer result in several disadvantages. One such disadvantage is that the acidic copolymers are polar and do not adsorb surfactants well, thus making them unstable and prone to coagulation or aggregation into larger particle. Another disadvantage is that the acidic core polymers have a high affinity for water. This affinity makes it difficult to encapsulate the core with the shell polymer because the core tends to remain at the polymer-water interface on the surface of the composite particle.

The present invention eliminates the instability, coagulation and encapsulation problems of polymers having relatively high levels of copolymerized acid in the core. Applicants have discovered that swellable, multi-stage polymer particles can be prepared by introducing a non-polymeric carboxylic acid to an earlier stage of the particles. By introducing a non-polymeric acid to an earlier stage after polymerization of said earlier stage, (preferably after polymerization of the complete, multi-

stage polymer) applicants have overcome the disadvantages of the core-shell polymers containing copolymerized acid in the core.

It is an object of the present invention to provide opacifying, multi-stage polymer particles having a non-polymeric carboxylic acid absorbed in an earlier stage of the particles. It is a further object of this invention to provide a process for making multi-stage polymer particles wherein the earlier-stage particles are relatively stable and easy to encapsulate.

SUMMARY OF THE INVENTION

This invention relates to opacifying, multi-stage polymer particles containing non-polymeric acid absorbed in an earlier stage and a process for making the polymer particles. The process comprises:

- (A) sequentially emulsion polymerizing polymer particles comprising two or more polymer stages wherein
  - (1) each of said polymer stages is emulsion-polymerized from a monomer system comprising one or more ethylenically-unsaturated monomer(s) containing one or more  $-\text{HC}=\text{C}<$  group(s);
  - (2) the final polymer stage of said particles has a glass transition temperature of about 50° C. or greater;
  - (3) at least one low-acid polymer stage, other than said final polymer stage, is prepared from a monomer system containing less than about 5% by weight of monomers containing carboxylic acid functionality;
  - (4) each polymer stage is different from any adjacent polymer stage by either about a one percent difference by weight in the amount of any ethylenically-unsaturated monomer used therein or by a difference in number-average molecular weight between said stage and said adjacent stage of at least about a factor of 2; and
  - (5) the polymer stages of said particles having a glass transition temperature of about 50° C. or greater comprise at least about 60% by weight of said particles;
- (B) contacting said polymer particles with a non-polymeric compound containing at least one carboxylic acid group before, during or after polymerization of said final polymer stage (2) to permit said acid-containing compound to be absorbed into said low-acid polymer stage (3); and
- (C) swelling the resulting polymer particles containing said absorbed acid-containing compound with water at or above the glass transition temperature of the next polymer or plasticized polymer of said final polymer stage (2) by contacting said polymer particles with base at a pH sufficient to swell said polymer particles, so as to produce particles which, when dried contain one or more void space(s) within said particles.

The polymer particles are useful as binders, opacifying agents and encapsulants.

DETAILED DESCRIPTION

The present invention involves multi-stage polymer particles containing void space(s) within said particles which are useful as binders, opacifiers in paint and coatings, and as encapsulants for chemically or biologically-active materials. The polymer particles are prepared by:

- (A) sequentially emulsion polymerizing polymer particles comprising two or more polymer stages wherein

(1) each of said polymer stages is emulsion-polymerized from a monomer system comprising one or more ethylenically-unsaturated monomer(s) containing one or more  $-\text{HC}=\text{C}<$  group(s);

(2) the final polymer stage of said particles has a glass transition temperature of about 50° C. or greater;

(3) at least one low-acid polymer stage, other than said final polymer stage, is prepared from a monomer system containing less than about 5% by weight of monomers containing carboxylic acid functionality;

(4) each polymer stage is different from any adjacent polymer stage by either about a one percent difference by weight in the amount of any ethylenically unsaturated monomer used therein or by a difference in number average molecular weight between said stage and said adjacent stage of at least about a factor of 2; and

(5) the polymer stages of said particles having a glass transition temperature of about 50° C. or greater comprises at least about 60% by weight of said particles;

(B) contacting said polymer particles with a non-polymeric compound containing at least one carboxylic acid group before, during or after polymerization of 25 said final polymer stage (2) to permit said acid-containing compound to be absorbed into said low-acid polymer stage (3); and

(C) swelling the resulting polymer particles containing said absorbed acid-containing compound with water at or above the glass transition temperature of the neat polymer or plasticized polymer of said final polymer stage (2) by contacting said particles with base at a pH sufficient to swell said polymer particles so as to produce particles which, when dried, contain 35 one or more void space(s) within said particles.

Each of the polymer stages is sequentially emulsion polymerized from a monomer system comprising one or more ethylenically-unsaturated monomers having one or more groups of the formula  $-\text{HC}=\text{C}<$ . As used herein, the term "stage" refers to the polymer formed during each sequence of polymerization, with the final stage being the last sequence of polymerization and earlier stages being the polymer formed during prior sequences of polymerization. Some suitable examples of ethylenically-unsaturated monomers are styrene, alpha-methylstyrene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, acrylamide, methacrylamide, acrylic acid and methacrylic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid or anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate, and various (C<sub>1</sub>-C<sub>20</sub>)alkyl or (C<sub>3</sub>-C<sub>20</sub>)alkenyl esters of (meth)acrylic acid. The expression (meth)acrylic acid is intended to serve as a 55 generic expression embracing both acrylic acid and methacrylic acid; e.g., methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate, and the like. Any of the polymer stages may optionally comprise as one component thereof a small amount of polyethylenically unsaturated monomer, such as ethylene glycol di(meth)acrylate, 65 allyl (meth)acrylate, 1,3-butanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, trimethylolpropane trimethacrylate, or divinylbenzene; the proportion thereof being in the range of about 0.1 to 20%, prefera-

ble 0.1% to about 3%, by weight based on the total monomer weight of said polymer stage.

Each of the polymer stages is different from any immediately adjacent polymer stage by either about a one percent difference by weight in the amount of any ethylenically-unsaturated monomer used therein, or by a difference of at least about a factor of 2 in number average molecular weight between said stage and said adjacent stage. Thus, the polymer stages are distinguishable by either the prescribed monomer difference or the prescribed molecular weight difference or both. Each or any stage contains the prescribed amount of one or more of said ethylenically-unsaturated monomers which is not present in the adjacent stage, or the adjacent stage contains the prescribed amount of said ethylenically-unsaturated monomers which is not present in stages immediately adjacent to it, or said adjacent stage contains about one percent more or less of one or more monomers which is present in stages adjacent to it. Alternatively or additionally, each or any stage has a number average molecular weight which is at least twice or less than one-half that of any adjacent stage. Adjacent polymer stage as used herein means a polymer stage which is immediately adjacent and which may be polymerized prior or subsequent to the stage referred to.

The polymer particles of this invention must contain at least one earlier polymer stage (3) which is prepared from a monomer system which contains less than about 30 5% by weight of monomer(s) containing carboxylic acid functionality. Preferably, the monomer system for this low-acid polymer stage contains less than 2% of monomer(s) having carboxylic acid functionality. High

levels of copolymerized carboxylic acid monomers in the earlier stages of these polymer particles have several disadvantages. One disadvantage is that the carboxylic acid copolymers are polar and do not adsorb surfactants effectively, thus, making them unstable and prone to coagulation or aggregation into undesirable larger particles. Additionally, the carboxylic acid-containing polymer stages have a high affinity for water which makes them difficult to encapsulate with other polymer stages. The present invention has overcome the above disadvantages by using little or no carboxylic acid monomer in this earlier polymer stage.

The final polymer stage (2) is also emulsion polymerized from a monomer system comprising one or more ethylenically-unsaturated monomer(s) containing one or more  $-\text{HC}=\text{C}<$  group(s). Examples of suitable monomer for the final polymer stage include the same monomers listed above for preparing the other polymer stages and as described in U.S. Pat. No. 4,427,836, which is herein incorporated by reference. The specific monomers used and the relative proportions thereof in any final polymer stage formed should be such that the final polymer stage is preferably permeable to bases. Similarly, any other polymer stage which is formed subsequent to said low-acid polymer stage (3) should preferably be permeable to bases to allow the bases to diffuse through to the low-acid polymer stage (3) in the subsequent neutralization step.

The final polymer stage (2) must have a T<sub>g</sub> of about 50° C. or greater, but the T<sub>g</sub> of the final polymer stage may be equal to, less than or greater than the T<sub>g</sub> of the earlier polymer stages. Preferably, at least one polymer stage which is formed subsequent to said low-acid polymer stage (3) has a higher T<sub>g</sub> than said low-acid polymer stage. Preferably the low-acid polymer stage (3)

has a Tg of about 150° C. or less; more preferably about 90° C. or less. The low-acid polymer stage (3) preferably has a number average molecular weight of about 10,000 or less. The polymer stages having a Tg of about 50° C. or greater cumulatively comprise at least about 60% by weight of the polymer particles.

The Tg of the polymer stages can be calculated using the Fox equation:

$$1/Tg(\text{polymer}) = W(a)/Tg(a) + W(b)/Tg(b) + \dots$$

where  $W(a)$  and  $W(b)$  are the weight fractions of comonomers (a) and (b) and  $Tg(a)$  and  $Tg(b)$  are the glass transition temperatures for homopolymers (a) and (b), respectively. Glass transition temperatures for various homopolymers are available in many literature sources, including J. Brandrup and E. H. Immergut, *Polymer Handbook* 2nd ed., John Wiley & Sons, New York, pp 139-192 (1975).

The first stage of emulsion polymerization in the process of the present invention may be the preparation of a seed polymer consisting of small dispersed polymer particles which are insoluble in the aqueous emulsion polymerization medium. This seed polymer provides particles of minute size which form the nuclei on which the subsequent polymer stages are formed.

As is common to aqueous emulsion polymers, there is used a water-soluble, free-radical initiator, such as hydrogen peroxide, tert-butyl hydroperoxide, or an alkali metal (sodium, potassium or lithium) or ammonium persulfate or a mixture of such an initiator with a reducing agent (such as a sulfite; more specifically an alkali metal metabisulfite, hydrosulfite, or hyposulfite, or sodium formaldehyde sulfoxylate) to form a redox system. The amount of initiator may be from 0.01 to about 2% by weight of the monomer charged and, in a redox system, a corresponding range (0.01 to about 2%) of reducing agent may be used. The temperature may be in the range of about 10° C. to 100° C. In the case of the persulfate systems, the temperature is preferably in the range of 60° C. to 90° C. In the redox system, the temperature is preferably in the range of about 30° to 70° C., more preferably about 40° to 70° C., most preferably in the range of about 55° to 70° C. The proportion of emulsifier may be zero, but, in the situation wherein a persulfate initiator is used, it can range up to about 5 weight percent, based on the weight of monomer charged to the first stage of polymerization. By carrying out the subsequent emulsion polymerization using a low level of emulsifier, the subsequent stages of polymer formation deposit the most-recently formed polymer on the existing dispersed polymer particles resulting from the preceding step or stage. As a general rule, the amount of emulsifier should be kept between 20% to about 60% of the amount theoretically required to saturate the surface of the polymer particles present in the reaction mixture at any given time as described in U.S. Pat. No. 2,520,959.

Any nonionic or anionic emulsifier may be used, either alone or in combination. Examples of nonionic emulsifiers include tert-octylphenoxyethylpoly(39)ethoxyethanol, dodecyloxypropoly(10)ethoxyethanol, nonylphenoxyethylpoly(90)ethoxyethanol, polyethylene glycol 2000 monooleate, ethoxylated castor oil, polyoxyethylene (20) sorbitan monolaurate, sucrose monococoate, di(2-butyl)phenoxypropoly(20)ethoxyethanol, hydroxyethylcellulosepolybutyl acrylate graft copolymer, dimethyl silicone polyalkylene oxide graft copolymer, poly(ethylene oxide)poly(butyl acrylate)

block copolymer, block copolymers of propylene oxide and ethylene oxide, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylated with 30 moles of ethylene oxide, N-polyoxyethylene(20)lauramide, N-lauryl-N-polyoxyethoxyethoxy(30)amine, and poly(10)ethoxyethylene glycol dodecyl thioether. Examples of anionic emulsifiers include sodium lauryl sulfate, sodium dodecylbenzene sulfonate, potassium stearate, sodium dioctyl sulfosuccinate, sodium dodecylphenyloxide disulfonate, nonylphenoxylethylpoly(10)ethoxyethyl sulfate ammonium salt, sodium styrene sulfonate, sodium dodecyl allyl sulfosuccinate, sodium or ammonium salts of phosphate esters of ethoxylated nonylphenol, sodium octoxynol-3-sulfonate, sodium cocoyl sarcosinate, sodium 1-alkyloxy-2-hydroxypropyl sulfonate, sodium alpha-olefin ( $C_{14}-C_{16}$ ) sulfonate, sulfates of hydroxylalkanols, tetrasodium N-(1,2-dicarboxy ethyl)-N-octadecylsulfosuccinate, disodium N-octadecylsulfosuccinate, disodium alkylamido polyethoxy sulfosuccinate, and disodium ethoxylated nonylphenol half ester of sulfosuccinic acid.

After the earlier polymer stage or stages are obtained, a subsequent stage or stages of emulsion polymerization is effected to form the final polymer stage on the earlier polymer stages particles. This may be performed in the same reaction vessel in which formation of earlier polymer stages were accomplished or the reaction medium containing the dispersed earlier stage particles may be transferred to another reaction container. It is generally unnecessary to add emulsifier unless a polymodal product is desired. The amount of polymer deposited to form the stages of polymer is generally such as to provide an overall size of the multi-stage polymer particle of about 0.07 to about 4.5 microns, preferably about 0.1 to about 3.5 microns, more preferably about 0.2 to about 2.0 microns, in unswollen condition (that is, before any neutralization to raise the pH to about 5 or higher). Preferably, the weight ratio of polymer stages having a Tg of about 50° C. or greater comprises at least about 80% by weight of the complete multi-stage polymer particles.

In one embodiment of this invention the multi-stage polymer particles are optionally encapsulated by additional polymer having a Tg of about 25° C. or less. Said additional polymer is prepared by emulsion polymerizing one or more ethylenically unsaturated monomer(s) in the presence of the multi-stage polymer. The same monomers as described earlier for preparing the earlier polymer stage can be used in preparing said additional polymer.

In carrying out the emulsion polymerization of the multi-stage polymer particles of this invention, reference can be made to U.S. Pat. No. 4,427,836 for specific process conditions.

Before, during or after polymerization of the final polymer stage (2), the polymer particles are contacted with a non-polymeric compound containing at least one carboxylic acid group for a sufficient period of time to allow the acid-containing compound to be absorbed into the low-acid polymer stage (3). The acid-containing compound should be added after adjusting the polymer composition to pH 4 or less to reduce the compound's solubility in the aqueous phase and increase its solubility in the polymer. Preferably, the acid-containing compound has a solubility in water greater than 0.001% and less than about 2% at pH 5 or less and at the Tg of the final polymer stage. This solubility range is

low enough to allow most of the acid-containing compound to absorb into the low-acid polymer stage, yet high enough so that it can diffuse through the aqueous phase to the polymer particles at a sufficient rate. Preferably, the amount of acid-containing compound to the weight of the complete multi-stage polymer particle ranges from about 1:2 to about 1:50.

Acid-containing compounds which are useful for this invention include C<sub>6</sub>-C<sub>12</sub> aliphatic or aromatic monocarboxylic acids, dicarboxylic acids, and mixtures thereof. Specific examples of acid-containing compounds are benzoic acid, m-toluic acid, p-chlorobenzoic acid, o-acetoxybenzoic acid, azelaic acid, sebatic acid, octanoic acid, cyclohexanecarboxylic acid, lauric acid, and monobutyl phthalate. The multi-stage polymer particles containing the non-polymeric acid absorbed in said low-acid polymer stage are swollen when the particles are subjected to a base, at or above the Tg of the neat polymer of Tg of the plasticized polymer of said final polymer stage, which permeates said final polymer stage and induces the polymer particles to swell with water. The amount of base used should adjust the pH of the polymer composition sufficiently to swell the polymer particles. Preferably the composition should be adjusted to a pH of 5.0 or greater, more preferably 6.0 or greater, and most preferably 7.0 or greater. When the water is removed by drying, the shrinkage of said low-acid polymer stage develops void spaces within the polymer particles. Preferred examples of base are ammonia; volatile lower aliphatic amines, such as trimethylamine and triethylamine; potassium hydroxide; sodium hydroxide; lithium hydroxide; calcium hydroxide; ammonium complexes of zinc, copper, or silver; strontium hydroxide and barium hydroxide.

If desired, the Tg of the neat polymer of the final polymer stage can be lowered during the swelling step to a "plasticized Tg" with a plasticizing solvent to facilitate swelling of the polymer particles upon treatment with base. The plasticizing solvent also aids in penetration of the polymer by the base. Suitable amounts of plasticizing solvents are about 1 to about 100 parts by weight based on 100 parts by weight of polymer. Suitable solvents are any which will plasticize the final polymer stage; for example, hexanol, ethanol, 3-hydroxy-2,2,4-trimethylpentyl isobutyrate, toluene, and the like and mixtures thereof. The solvent can be added either before, after or with the addition of the base. In certain causes the monomer system itself can function as the plasticizing solvent for the polymer.

After being expanded by water to the desired extent, the swollen particles are cooled to a temperature below the Tg of said final polymer stage. The water is then removed from the particles by drying at the lower temperature, resulting in the formation of microvoids within the particles. For best results, the water is removed rapidly from the polymer particles. Slow drying at high humidity may be detrimental to microvoid formation. The multi-stage polymer particle dispersions of the present invention are useful in aqueous coating and impregnating compositions as opacifying agents in such compositions. They are useful either as a supplement to, or replacement of, pigmentary matter and/or extenders therefor. For these purposes, the aqueous dispersions of the multi-stage polymer particles may be added directly to the coating and/or impregnating compositions. Alternatively, the multi-stage polymer particles may be isolated from the dispersions and dried to make them free-flowing in character so that they can be packaged,

sold and shipped or stored before use. The dry powder thus obtained can also be used in coatings based on organic solvents provided the final polymer stage of the multi-stage polymer particles is not soluble in the organic solvent.

Besides being useful in water-based paints based on vinyl or acrylic polymer latices or aqueous solutions of vinyl or acrylic polymers (to replace all or part of opacifying pigments heretofore used, especially those of titanium dioxide), the microvoid-containing particulate polymers of the present invention may be used for similar purposes in other coating systems. These include resin-forming condensation products of thermosetting type, such as phenoplasts and aminoplasts, including urea-formaldehyde and melamine-formaldehyde, and other condensates (e.g., water-dispersible alkyd resins). In addition, polymodal heteropolymers of the present invention having a predominant proportion of the microvoid-containing large mode and a relatively minor proportion of a small mode, but also provide an adhesion-promoting action by way of the small mode.

The following examples are presented to further illustrate this invention. The examples are intended to be illustrative and are not limitative of the present invention. All parts and percentages are by weight unless otherwise indicated.

#### EXAMPLE I—PREPARATION OF POLY(ISOBUTYL METHACRYLATE) LOW-ACID STAGE

A 3-liter, round-bottomed flask with 4 necks was fitted with reflux condenser, paddle stirrer, thermometer and nitrogen inlet. 1500 grams of deionized water were added to the flask and stirred under a nitrogen atmosphere at 85° C. To the deionized water were added 3 grams of sodium persulfate and 40 grams of an acrylic seed latex having a 46.5% solids content and an average diameter of 95 nanometers. A monomer emulsion (140 g. of water, 6 g. of 23% sodium dodecylbenzenesulfonic acid, 360 g. of isobutyl methacrylate and 40 g. of n-dodecyl mercaptan) was added over 2 hours along with 3 g. of sodium persulfate dissolved in 80 g. of water. The resultant latex was held at 85° C. for 30 minutes, cooled and filtered. The resultant low-acid stage polymer latex had an 18.7% solid content, average particle diameter of 260 nanometers and a number average molecular weight of 2000 as measured by gel permeation chromatography.

#### EXAMPLE II—PREPARATION OF MULTI-STAGE POLYMER PARTICLES WITH BENZOIC ACID ABSORBED IN LOW-ACID STAGE BEFORE POLYMERIZATION OF FINAL STAGE

To 470 g. of deionized water, stirred under nitrogen in a flask equipped as in Example 1, was added 50 g. of the low-acid stage polymer latex from Example 1 along with 20 g. of benzoic acid. The mixture in the flask was heated to 80° C. and then 1.2 g. of sodium persulfate dissolved in 10 g. of water was added. A monomer mixture of 46 g. of butyl methacrylate, 66.7 g. of methyl methacrylate and 2.3 g. of methacrylic acid was added slowly over a one-hour period to give a second polymer stage. After a 10-minute hold at 80° C. to complete the polymerization, 115 g. of styrene were added over a one-hour period to form the final polymer stage. Then 20 g. of 28% aqueous ammonia were added to swell the particles and the temperature was raised to 85° C. for 30

minutes followed by cooling and filtration. The final latex product had a 28.9% solids content and pH of 9.4. Diluted latex was dried on a microscope slide and immersed in hydrocarbon oil ( $n_D=1.51$ ) and examined with an optical microscope at 900X. A single air void can be seen inside each particle as a dark circle. The swollen multi-stage polymer latex was incorporated into a film to measure the Kubelka-Munk scattering coefficient (S/mil) as described in U.S. Pat. No. 4,427,836. S/mil of the resultant film was 0.12.

**EXAMPLE III—PREPARATION OF  
MULTI-STAGE POLYMER PARTICLES WITH  
BENZOIC ACID ABSORBED IN LOW-ACID  
STAGE DURING POLYMERIZATION OF  
FINAL STAGE**

Multi-stage polymer particles were prepared following the procedures of Example II, except that the benzoic acid was mixed with styrene and this mixture was added to the flask over a one-hour period. The resulting latex product had a 28.3% solids content, pH of 9.9 and S/mil of 0.16. Voids were noticeable in the dry polymer particles through examination under a microscope.

**EXAMPLE IV—PREPARATION OF  
MULTI-STAGE POLYMER PARTICLES WITH  
BENZOIC ACID ABSORBED IN LOW-ACID  
STAGE AFTER POLYMERIZATION OF FINAL  
STAGE**

Multi-stage polymer particles were prepared following the procedures of Example II, except that the benzoic acid was added to the flask immediately after addition of the styrene was complete. When the ammonia was added, the latex became thick and 100 grams of water were added. The resulting latex product had a 23.3% solids content, pH of 9.7 and S/mil of 0.13. Examination of dry polymer particles under a microscope showed a single void in each particle.

**EXAMPLE V—PREPARATION OF  
MULTI-STAGE POLYMER PARTICLES  
HAVING BUTYL METHACRYLATE EARLIER  
STAGE AND AZELAIC ACID ABSORBED  
THEREIN**

A low molecular weight, earlier stage latex was prepared following the procedures of Example I, except that 50 grams of an acrylic latex seed (41.3% solids, average diameter 57 nm) were used and isobutyl methacrylate was replaced with an equal amount of butyl methacrylate. The resulting latex has an 18.8% solids content and an average particles diameter of 150 nm.

This earlier stage latex as then used to prepare multi-stage polymer particles following the procedures of Example II, except that the amount of initial deionized water was increased to 700 grams and benzoic acid was replaced with azelaic acid. The resulting multi-stage latex product had a 23.8% solids content, pH of 9.4, average particle diameter of 470 nm, and S/mil of 0.20.

**EXAMPLE VI**

A high molecular weight earlier stage latex was prepared following the procedures of Example V, except that the n-dodecyl mercaptan was excluded. The resulting latex had a 17.4% solids content and an average particle diameter of 156 nm.

This earlier stage latex was then used to prepare multi-stage polymer following the procedures of Example V. The resulting multi-stage latex product had a

24.4% solids content, pH of 9.2, average particle diameter of 482 nm, and S/mil of 0.15.

**EXAMPLE VII—PREPARATION OF  
MULTI-STAGE POLYMER PARTICLES  
HAVING BUTYL ACRYLATE EARLIER STAGE**

Multi-stage polymer particles were prepared following the procedures of Example VI except that butyl methacrylate in the earlier stage was replaced with an equal amount of butyl acrylate. The resulting multi-stage latex product had a 23.4% solids content, pH of 9.4, average particle diameter of 503 nm and S/mil of 0.11.

**EXAMPLE VIII—PREPARATION OF  
MULTI-STAGE POLYMER PARTICLES  
HAVING METHYL METHACRYLATE  
EARLIER STAGE**

Multi-stage polymer particles were prepared following the procedures of Example V, except that butyl methacrylate in the earlier stage was replaced with an equal amount of methyl methacrylate. The resulting multi-stage latex product had a 24.0% solids content, pH of 9.3, average particle diameter of 477 nm, and S/mil of 0.08. The earlier polymer stage had an estimated Tg of 75° C.

**EXAMPLE IX—PREPARATION OF  
MULTI-STAGE POLYMER PARTICLES  
HAVING STYRENE EARLIER STAGE**

Multi-stage polymer particles were prepared following the procedures of Example V, except that butyl methacrylate in the earlier stage was replaced with an equal amount of styrene. The resulting multi-stage latex product had a 24.1% solids content, pH of 9.3, average particle diameter of 389 nm, and S/mil of 0.11. The earlier polymer stage had a measured Tg of 70° C. by differential scanning calorimetry.

We claim:

1. A process for preparing opacifying polymer particles containing one or more void space(s) within said particles comprising:
  - (A) sequentially emulsion polymerizing polymer particles comprising two or more polymer stages wherein
    - (1) each of said polymer stages is emulsion-polymerized from a monomer system comprising one or more ethylenically-unsaturated monomer(s) containing one or more  $-\text{HC}=\text{C}<$  group(s);
    - (2) the final polymer stage of said particles has a glass transition temperature of about 50° C. or greater;
    - (3) at least one essentially low-acid, earlier polymer stage, other than said final polymer stage (2), is prepared from a monomer system which contains less than about 5% by weight of monomers containing carboxylic acid functionality;
    - (4) each polymer stage is different from any adjacent polymer stage by either about a one percent difference by weight in the amount of any ethylenically unsaturated monomer used therein or by a difference in number average molecular weight between said stage and said adjacent stage of at least about a factor of 2; and
    - (5) the polymer stages of said particles having a Tg of about 50° C. or greater comprises at least about 60% by weight of said particles;
  - (B) contacting said polymer particles with a non-polymeric aliphatic or aromatic carboxylic acid(s)

having 6 to 12 carbon atoms containing at least one carboxylic acid group before, during or after polymerization of said final polymer stage (2) to permit said acid-containing compound to be absorbed into said low-acid polymer stage (3); and

(C) swelling the resulting multi-stage polymer particles containing said absorbed acid-containing compound with water, an optical plasticizing solvent, at or above the glass transition temperature of the neat polymer or glass transition temperature of the optionally plasticized polymer of said final polymer stage (2) by contacting said particles with base at a pH sufficient to swell said polymer particles, so as to produce particles which, when dried, contain one or more void space(s) within said particles.

2. A process of claim 1 wherein said low-acid polymer stage (3) has a glass transition temperature of about 150° C. or less.

3. A process of claim 1 wherein said low-acid polymer stage (3) has a glass transition temperature of about 90° C. or less.

4. A process of claim 1 wherein said low-acid polymer stage (3) has a number average molecular weight of about 10,000 or less.

5. A process of claim 1 wherein said polymer stages having a Tg of about 50° C. or greater comprises at least about 80% by weight of said particles.

6. A process of claim 1 wherein said non-polymeric, acid-containing compound has a solubility in water of about 2% of less by weight at the glass transition temperature of said final polymer stage (2), and the amount of said acid-containing compound to the weight of said multi-stage polymer particles is about 1:2 to about 1:50.

7. A process of claim 6 wherein said non-polymeric, acid-containing compound is selected from C<sub>6</sub>-C<sub>12</sub> aliphatic or aromatic mono- and dicarboxylic acids.

8. A process of claim 6 wherein said non-polymeric, acid-containing compound is selected from benzoic acid, m-toluic acid, p-chlorobenzoic acid, o-acetoxybenzoic acid, azelaci acid, sebacic acid, octanoic acid, cyclohexanecarboxylic acid, lauric acid, and monobutyl phthalate.

9. A process of claim 1 wherein said ethylenically-unsaturated monomer(s) are selected from styrene, alpha-methylstyrene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, acrylamide, methacrylamide, acrylic acid, methacrylic acid, acryloxypropionic acid, methacryloxypropionic acid, itaconic acid,aconitic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate, and (C<sub>1</sub>-C<sub>20</sub>) alkyl or (C<sub>3</sub>-C<sub>20</sub>) alkenyl esters of acrylic and methacrylic acid.

10. A process of claim 1 wherein said low-acid polymer stage (3) is prepared from a monomer system which contains essentially no monomer(s) having carboxylic acid functionality.

11. A process of claim 1 wherein said multi-stage polymer particles are further encapsulated by additional polymer having a glass transition temperature of less than about 50° C. by emulsion polymerizing one or more ethylenically unsaturated monomer(s) containing one or more -HC=C< group(s) in the presence of said multi-stage polymer particles.

12. A process of claim 11 wherein said additional polymer has a Tg of about 25° C. or less.

13. A process of claim 1 wherein said base is selected from ammonia; potassium hydroxide; sodium hydroxide; lithium hydroxide; calcium hydroxide; strontium hydroxide; barium hydroxide; volatile lower aliphatic amines; and ammonium complexes of zinc, copper and silver.

EXHIBIT T



US005989331A

**United States Patent**

[19]

Bauer et al.

[11] **Patent Number:** 5,989,331[45] **Date of Patent:** \*Nov. 23, 1999[54] **TIO<sub>2</sub> SLURRY STABILIZATION**

[75] **Inventors:** Carl J. Bauer; John D. Boothe, both of Gonzales, Tex.; Frank S. Scimecca, Newtown, Pa.; Dwaine E. Siptak, Gonzales, Tex.

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[\*] **Notice:** This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

This patent is subject to a terminal disclaimer.

[21] **Appl. No.:** 08/861,589

[22] **Filed:** May 22, 1997

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[51] **Int. Cl.:** C09C 3/06; C09C 1/36; C04B 14/10

[52] **U.S. Cl.:** 106/444; 106/468; 106/462; 106/486; 106/487

[58] **Field of Search:** 106/444, 462, 106/468, 486, 487

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[57] **ABSTRACT**

A stable aqueous pigment slurry and a process for preparing same. The slurry contains about 50 to 90 wt. %, based on the weight of the slurry, of a pigment such as titanium dioxide and about 0.2 to 3.0 wt. %, based on the weight of the slurry, of a smectite clay such as bentonite, hectorite or montmorillonite. Preferably, the pigment slurry also contains about 0.1 to 2.0 wt. %, based on the weight of the slurry, of a dispersant. The process involves admixing a pigment slurry and a smectite clay slurry and preferably also the dispersant by milling the three components together under high shear conditions.

20 Claims, No Drawings

TiO<sub>2</sub> SLURRY STABILIZATION

## CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of provisional patent application Ser. No. 60/018,411 filed May 28, 1996.

## FIELD OF THE INVENTION

The invention relates to stable aqueous pigment slurries and processes for preparing same. The stabilized pigment, e.g. TiO<sub>2</sub>, slurries of the invention exhibit dramatically reduced syneresis and settling out.

## BACKGROUND OF THE INVENTION

When any pigment such as TiO<sub>2</sub> is dispersed in water, there is a tendency for the pigment to immediately start to flocculate. One prior art approach to overcome such problem is to use surfactants. However, the present trend is to avoid, if at all possible, the use of surfactants. Guar gums have been used with some pigment slurries to help prevent settling. Although guar gums are helpful in reducing the settling-out problem, such approach is not efficient. Intermittent stirring in the storage tank is still required and the presence of the guar gums renders the slurry open to enzyme attack.

## SUMMARY OF THE INVENTION

It has now been found that it is possible to prepare stable aqueous pigment slurries, especially TiO<sub>2</sub> slurries, which have a marked resistance to settling out and syneresis. The stable slurries of the invention do not require significant amounts of dispersants and need not be continuously or intermittently stirred to overcome settling out and syneresis while in the storage tank.

The pigment slurries of the invention comprise an admixture of the pigment (preferably titanium dioxide) and a smectite clay. One or more dispersants are also preferably present to wet-out the pigment; however, syneresis and settling-out control are not as dependent on the dispersant when a smectite clay is present.

## DETAILS OF THE INVENTION

The invention encompasses a stable aqueous pigment slurry comprising an admixture of about 50 to 90 wt. %, preferably 60 to 85 wt. %, based on the weight of the slurry of a pigment and about 0.2 to 3 wt. %, preferably 0.5 to 2.5 wt. %, based on the weight of the slurry, of a smectite clay. Preferably, the smectite clay is a naturally-occurring or synthetic bentonite, hectorite or montmorillonite clay.

Preferably, the pigment comprises titanium dioxide which is present in an amount of 60 to 85 wt. %, based on the weight of the slurry.

The average particle size of the smectite clay in the final slurry will typically be in the range of about 0.025 to 1.0 $\mu$ , and the average particle size of the titanium dioxide in the final slurry will typically be in the range of about 0.25 to 0.5 $\mu$ . Such average particle size ranges may be achieved by admixing the titanium dioxide with the smectite clay and milling the admixture under high shear conditions, as more particularly described below.

Preferably, the pigment slurry will also contain one or more dispersants, present in an amount of about 0.1 to 2.0 wt. %, based on the weight of the slurry. Useful dispersants include alkali polyphosphates, aliphatic carboxylic acids and alkali salts thereof, polyacrylic acids and alkali salts thereof, polyhydroxy alcohols, amino alcohols and mixtures thereof.

The stable pigment slurry of the invention is preferably prepared by admixing the pigment, e.g. titanium dioxide,

with an aqueous slurry of the smectite clay containing 5 to 20 wt. % and preferably 8 to 12 wt. % of smectite clay based on the weight of the aqueous smectite clay slurry. Such admixing is readily accomplished by milling (or grinding) the components under conditions such that the average particle size of the smectite in the final slurry will be in the range of about 0.025 to 1.0 $\mu$ , and the average particle size of the titanium dioxide in the final slurry will be in the range of about 0.2 to 0.5 $\mu$ . Suitable admixing techniques for achieving such average particle sizes are well known in the prior art, e.g. mechanical grinding, steam milling, micronization, high shear milling, ball milling, pug milling, disc milling, dispersion, colloidal milling, Manton-Gaulin milling, horizontal media milling, etc.

The invention is illustrated by the following Example which to be considered as illustrative and not delimiting of the invention otherwise described.

## EXAMPLE I

A titanium dioxide slurry having 76.2 wt. % solids was admixed with the smectite clay slurries (10 wt. % solids) in the weight %, based on the weight of the final slurry, indicated in Formulation I below. "Gelwhite L" is a smectite clay of the montmorillonite type available from Southern Clay Products, Inc.; it is a fine powder having a GEB brightness of 83, a moisture content of 10%, a pH of 9.0 and a viscosity of 525 cps (10% solids, Brookfield, 20 RPM). "Bentolite L-10" is a naturally occurring off-white calcium bentonite having a moisture content of 8%, a pH of 7.5 (10% slurry) and a loose bulk density of 30.0 lb/ft<sup>3</sup>. "HSD" signifies high shear dispersing; "M-G" signifies milling by hand using the Manton-Gaulin mill.

## FORMULATION I

No.	Smectite	Weight % Smectite	Mixing Process
A	None	None	2600 rpm, 40 mm blade, HSD, 5 min
B	Gelwhite L	1	3000 rpm, 40 mm blade, HSD, 5 min
C	Gelwhite L	1	3000 rpm, 40 mm blade, HSD, 5 min then hand M-G
D	Gelwhite L	2	4000 rpm, 40 mm blade, HSD, 5 min
E	Gelwhite L	1	3000 rpm, 40 mm blade, HSD, 5 min
F	Gelwhite L	1	3000 rpm, 40 mm blade, HSD, 5 min then hand M-G
G	Gelwhite L	1	3000 rpm, 40 mm blade, HSD, 5 min
X	Bentolite L-10	1	3000 rpm, 40 mm blade, HSD, 5 min

The Formulation I slurries were examined for syneresis at 55° C. after 10 and 27 days and contrast ratios and y reflectance values of paint formulations prepared from the slurries. The results are shown in Table I.

TABLE I

No.	Syneresis, %		Contrast	y Reflectance
	10 days	26 days	Ratio, %	Value
A	8.93	12.5	97.98	94.14
B	0.00	0.00	98.38	94.40
C	0.00	0.00	98.49	94.70
D	0.00	0.00	100.00	96.79
E	0.00	0.00	98.65	95.07
F	0.00	0.00	98.74	95.01
G	1.85	5.61	98.62	94.71
X	<1.00	<1.00	98.76	95.07

## EXAMPLE II

A titanium dioxide slurry was prepared from the ingredients set forth in Formulation II below. "Polywet ND-2" is an

anionic dispersant obtained from Uniroyal Corporation.  
"Bubblebreaker 748" is a silicone defoamer.

## EXAMPLE 3

<u>FORMULATION II</u>	
Ingredient	Weight, grams
Water	210.18
NaOH	0.23
Potassium tripolyphosphate	3.00
Polywet ND-2	2.13
Bubblebreaker 748	0.06
Thickener	As indicated in Table II
Biocide	0.39
Titanium dioxide	354.00

Paint formulations were prepared from the Formulation II slurries by adding 100 grams of the slurry to 59.0 grams of paint base and mixed. The paint base consisted of 40.0 grams of "UCAR 376" Latex resin, a vinyl-acrylic resin obtained from Union Carbide Corporation; 1.4 grams of "Texanol" (a high molecular weight alcohol); 0.3 gram of "Bubblebreaker 748"; 0.3 gram of "Triton CF-10" (a non-ionic surfactant having an HLB value of about 13); and 17.0 grams of water. Paint formulations employing Formulations III, IV and V described below were prepared in the same manner. Table II set forth below contains the results obtained from the use of Formulation II.

5 A titanium dioxide slurry was prepared from the ingredients set forth in Formulation III below. "Tamol 1124" is a sodium carboxylate dispersant and "AMP 95" is 2-amino-2-methyl-1-propanol.

<u>FORMULATION III</u>	
Ingredient	Weight, grams
Water	140.60
Thickener	As indicated in Table III
Tamol 1124	0.53
AMP 95	1.28
Titanium dioxide	450.00

20 The ingredients in Formulation III were mixed on a high-speed disperser for 10 minutes and thereafter were dispersed in a media mill for 30 minutes (1,000 rpm) using glass beads. Table III set forth below contains the results obtained from the use of Formulation III.

TABLE II

Sample	Thickener/ Amount	Brookfield Viscosity, 60 rpm #3 spindle		% Syneresis/ 10 days, 50° C.		Hegman Grind	Contrast Ratio	Reflectance Value
		10 days	30 days, 50° C.	34 days/30° C.	30 days, 50° C.			
A	BT11/0.0054%	362	1.5	<2/some	7.5+	97.85	93.13	
B	BT11/1.0%	10,000+	0	0/none	7+	99.35	95.33	
C	BT11/0.5%	2,650	0	0/none	7.5+	99.54	95.05	
D	BT11/0.25%	960	0	0/none	7.5+	99.66	95.06	
E	None	200	3.5	5/severe	7.5+	98.10	93.57	
AA	BT11/0.0054%	204	1.5	5/some	7.5+	98.49	94.26	
BB	BL10/1.0%	470	1	<1/none	7.5+	99.45	95.25	
CC	BL10/0.5%	300	2.0	<2/some	7.5+	99.10	94.74	
DD	BL10/0.25%	224	3.3	3/severe	7.5	98.98	94.59	
EE	BL10/0.5%	320	1.7	<2/some	7.5+	99.56	94.99	
FF	BL10/0.0054%	252	3.2	3.2/severe	7.5+	98.41	94.16	
GG	BL10/1.5%	594	0.5	0/none	7.5+	99.37	96.54	
HH	BL10/1.75%	736	0	0/none	7.5+	99.13	96.13	

All percentages of thickener are based on the weight of titanium dioxide added to the slurry, not the entire slurry weight.

"BT11" is a 50:50 blend of hectorite and hydroxyethylcellulose.

"BL10" is a naturally occurring off-white calcium bentonite having a moisture content of 8%, a pH of 7.5 (10% slurry) and a loose bulk density of 30.0 lb/ft<sup>3</sup>.

TABLE III

Sample	Thickener/ Amount	Brookfield Viscosity, 60 rpm #3 spindle		% Syneresis, 10 days/30 days, 50° C.	Settling, 30 days, 50° C.	Hegman Grind	Contrast Ratio	Reflectance Value
		10 days	30 days, 50° C.					
183A	BT10/1%	650	0/0	some	7.5+	98.66	94.21	
183B	BL10/0.5%	316	1/1	some	7.5+	98.68	94.51	
183C	BL10/0.75%	346	0.5/0.5	some	7.5+	98.87	94.49	
183D	BL400/1%	356	0/0	some	7.5+	97.87	93.80	

TABLE III-continued

Sample	Thickener/ Amount	Brookfield Viscosity, 60 rpm #3 spindle	% Syneresis, 10 days/30 days, 50° C.	Settling, 30 days, 50° C.	Hegman Grind	Contrast Ratio	Reflectance Value
183E	BLWH/0.5%	500	0.5/0.5	slight	7.5+	98.50	94.27
183F	BLWH/0.75%	740	0/0	slight	7.5+	98.25	92.76
183G	BL400/0.75%	278	1/0.5	some	7.5+	98.41	94.20
184A	3X/0.5%	430	0/0	some	7.5+	98.79	94.77
184B	SCPX944/0.5%	524	0/0	some	7.5+	99.77	94.67
184C	3X/0.75%	646	1.7	some	7.5+	99.78	94.60
182A-1	None	166	8.6/8.7	hard	7.5+	98.79	94.58
001D	None	174	11.7/20.3	hard	7.5+	94.31	91.62

All percentages of thickener are based on the weight of titanium dioxide added to the slurry, not the entire slurry weight.

"BL10" is a naturally occurring off-white calcium bentonite having a moisture content of 8%, a pH of 7.5 (10% slurry) and a loose bulk density of 30.0 lb/ft<sup>3</sup>.

"BLWH" is a sodium ion-exchanged version of BL10.

"BL400" is a micronized version of BLWH.

"3X" is a Wyoming bentonite slurry milled 3 times in a Manton-Gaulin mill.

"SCPX" is 3X-treated with a quaternary ammonium compound.

## EXAMPLE 4

A titanium dioxide slurry was prepared from the ingredients set forth in Formulation IV below.

25 Titanium slurries were prepared to illustrate the effect of different dispersants. The ingredients are shown in Formulation 5:

## FORMULATION IV

Ingredient	Weight, grams	30
Water	140.0	
Thickener	As indicated in Table IV	
Titanol 1124	0.9	
Potassium tripolyphosphate	0.6	
AMP-95	1.5	
Bubblebreaker 748	0.6	
Titanium dioxide	350.0	

The ingredients in Formulation IV were mixed on a high-speed disperser for 10 minutes and thereafter were dispersed in a media mill for 30 minutes (1,000 rpm) using glass beads. Table IV set forth below contains the results obtained from the use of Formulation IV.

40 The ingredients in Formulation IV were mixed on a high-speed disperser for 10 minutes and thereafter were dispersed in a media mill for 30 minutes (1,000 rpm) using glass beads. Table V set forth below contains the results obtained from the use of Formulation V.

## TABLE IV

Sample	Thickener/ Amount	Brookfield Viscosity, 60 rpm #3 spindle	% Syneresis, 10 days/31 days, 50° C.	Settling, 31 days, 50° C.	Hegman Grind	Contrast Ratio	Reflectance Value
185A	BL10/0.64%	858	0/0	none	7+	96.11	90.25
185B	BL10/0.32%	880	0/0	none	7+	96.54	90.50
185C	BL10/0.96%	860	0/0	none	7+	97.47	91.52
185D	BLWH/0.64%	1,028	0/0	none	7+	97.22	91.17
185E	BLWH/0.32%	948	0/0	none	7+	97.00	91.24
185F	BL400/0.64%	832	0/0	none	7+	97.00	91.09
185G	BL400/0.96%	888	0/0	none	7+	96.93	91.27
185H	3X/0.64%	1,240	0/0	none	7+	97.78	92.03
185I	3X/0.32%	1,014	0/0	none	7+	96.55	90.86
185J	None	1,318	0/0	none	7+	97.03	91.51
185K	None	1,040	0/0	none	7+	96.34	90.67
185L	None	602	0/0	none	7+	96.04	90.27
185M	SCPX944/0.25%	1,712	0/0	none	7	97.41	91.32
185N	BL10/0.64%	932	0/0	none	—	—	—
185O	BLWH/0.32%	948	0/0	none	—	—	—
001C	BL10/1.0%	610	8.3/12.7	slight	7	96.37	93.59
001E	None	270	18.5/25.5	hard	7	90.12	87.06

All percentages of thickener are based on the weight of titanium dioxide added to the slurry, not the entire slurry weight.

TABLE V

Sample grams	Surfactant/ Amount, grams	Thickener/ Amount, grams	Brookfield Visc., 60 rpm, #3	% Syneresis 10 days/20 days, 50° C.	Settling 20 days, 50° C.
190A	TSG-1/0.71	none	226	3.4/5.1	slight
190E	TSG-1/1.42	none	972	—	—
190H	TSG-1/0.71	BL10/2.25	988	<0.5/<0.5	none
190B	S104/0.52	none	112	7/8.6	some
190F	S104/1.04	none	564	—	—
190G	S104/0.52	BL10/2.25	958	0.5/0	none
190C	T165/1.14	none	192	5.6/4.6	slight
190D	T165/2.28	none	374	—	—
190I	T165/1.14	BL10/2.25	908	0/0	none

"TSG-1" is "Tanol SG-1", an anionic surfactant.  
"S-104" is "Surfonly", a hydrophobic surfactant.  
"T165" is "Tanol 165", a nonionic surfactant.

What is claimed is:

1. A stable aqueous pigment slurry comprising an admixture of:

- (a) about 50 to 90 wt. %, based on the weight of the slurry, of a pigment; and
- (b) about 0.2 to 3.0 wt. %, based on the weight of the slurry, of a smectite clay.

2. The slurry of claim 1 further comprising about 0.1 to 2.0 wt. %, based on the weight of the slurry, of a dispersant.

3. The slurry of claim 2 wherein the dispersant is selected from the group consisting of alkali polyphosphates, aliphatic carboxylic acids and alkali salts thereof, polyacrylic acid and alkali salts thereof, polyhydroxy alcohols, amino alcohols and mixtures thereof.

4. The slurry of claim 1 wherein the pigment is present in an amount of 60 to 85 wt. %, based on the weight of the slurry.

5. The slurry of claim 1 wherein the pigment comprises titanium dioxide.

6. The slurry of claim 4 wherein the average particle size of the titanium dioxide is in the range of about 0.2 to 0.5 $\mu$ .

7. The slurry of claim 1 wherein the smectite clay is present in an amount of 0.5 to 2.5 wt. %, based on the weight of the slurry.

8. The slurry of claim 1 wherein the average particle size of the smectite clay is in the range of about 0.025 to 1.0 $\mu$ .

9. The slurry of claim 1 wherein the smectite clay is selected from the group consisting of bentonite, hectorite and montmorillonite clays.

10. A process for preparing a stable aqueous pigment slurry which comprises admixing about 50 to 90 wt. %, based on the weight of the pigment slurry, of a pigment with about 0.2 to 3.0 wt. %, based on the weight of the pigment slurry, of a smectite clay, said smectite clay being present in the form of an aqueous smectite clay slurry containing about 5 to 20 wt. % smectite clay, based on the weight of the aqueous smectite clay slurry.

11. The process of claim 10 wherein about 0.1 to 2.0 wt. %, based on the weight of the pigment slurry, of a dispersant is also present during the admixing.

12. The process of claim 11 wherein the dispersant is selected from the group consisting of alkali polyphosphates, aliphatic carboxylic acids and alkali salts thereof, polyacrylic acid and alkali salts thereof, polyhydroxy alcohols, amino alcohols and mixtures thereof.

13. The process of claim 10 wherein the pigment is present in an amount of 60 to 85 wt. %, based on the weight of the pigment slurry.

14. The process of claim 10 wherein the pigment comprises titanium dioxide.

15. The process of claim 10 wherein the smectite clay is present in the aqueous smectite clay slurry in an amount of 8 to 12 wt. %, based on the weight of the aqueous smectite clay slurry.

16. The process of claim 10 wherein the smectite clay is present in an amount of 0.5 to 2.5 wt. %, based on the weight of the pigment slurry.

17. The process of claim 10 wherein the admixing of the pigment, dispersant and aqueous smectite clay slurry is accomplished by milling under high shear conditions.

18. The process of claim 17 wherein the pigment comprises titanium dioxide and the milling is carried out such that the average particle size of the titanium dioxide is in the range of about 0.2 to 0.5 $\mu$ .

19. The process of claim 10 wherein the milling is carried out such that the average particle size of the smectite clay is in the range of about 0.025 to 1.0 $\mu$ .

20. The process of claim 10 wherein the smectite clay is selected from the group consisting of bentonite, hectorite and montmorillonite clays.

\* \* \* \* \*

EXHIBIT

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(12) Patent:

(11) CA 935255

(54) HIGH-SOLIDS TIO2 PIGMENT AND METHOD FOR MAKING SAME

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### ABSTRACT:

CLAIMS: Show all claims

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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Last Modified: 2002-12-31

[Important Notices](#)

Titanium dioxide pigment for use in coating compositions, rubber, paper and the like has for years been produced by the so-called sulfate process or the chloride process, as the case may be, and in either case the finished pigment is in the form of a finely divided dry powder which is bagged for shipment. Usually large scale commercial operations will require a large inventory of various grades of bagged pigment which necessitates huge storage sheds and handling equipment for stacking the bags and carrying the stacked bags from storage to transportation facilities such as trucks or railroad cars. This multiple handling of the bagged pigment inevitably results in losses from broken bags. Moreover a similar situation exists at the customer end, i.e., bag breakage with loss of pigment. Further, it is well recognized that the effectiveness of a pigment in coating compositions, as an additive in paper manufacture and the like depends in large measure on how well the pigment disperses in the particular medium to which it is added. When the pigment is shipped in bags the customer must not only empty the individual bags by hand but also must add one or more dispersing agents to his particular formulation. The dispersion of finely divided solids and in particular titanium dioxide pigment in liquid media involves phenomena which are only partially understood even by research chemists and consequently for most customers the problem of effecting optimum dispersion of the pigmentary  $TiO_2$  in a given liquid is largely one of trial and error.

The pumpable high-solids  $TiO_2$  pigment slurry of this invention comprises anatase or rutile  $TiO_2$  pigment uniformly dispersed in a medium which may be water, a solvent or combination of water and solvent plus organic reagents selected to impart desirable properties to the slurry such as suspension, freedom from foaming, resistance to biological degradation and suitable viscosity for handling purposes.

The  $TiO_2$  pigment may be a dry, finished pigment prepared



by the sulfate or the chloride process, as the case may be, and treated with various metal oxides such as  $Al_2O_3$ ,  $TiO_2$ ,  $ZrO$ , and  $SiO_2$ ; or may be a dry or wet pigment-intermediate i.e. treated or untreated calciner discharge. The percentage of  $TiO_2$  pigment contained in the slurry is, in keeping with the objects of this invention, relatively high, 50% and preferably 60% being the lower limit and from 75-80% being the upper limit, the latter being dependent upon such factors as the water and/or oil demand of the  $TiO_2$  pigment used, and the degree of dilatancy that can be tolerated at acceptable pumping rates. For the expected uses of the  $TiO_2$  pigment slurry of this invention the  $TiO_2$  pigment slurries would generally be shipped at from 60-80% solids on a  $TiO_2$  weight basis. The slurry is prepared by adding the  $TiO_2$  pigment with vigorous agitation to an aqueous or solvent medium or mixtures thereof, containing a combination of one or more dispersing agents, a thickening agent and optionally a defoamer and a mildewcide. The dispersing agents are di-polar compounds of high molecular weight, typical dispersants being the polyphosphates such as potassium tripolyphosphate and sodium hexametaphosphate; and amines such as triethanolamine or monoisopropanolamine. The thickening agent serves to inhibit settling and add the desired viscosity characteristics to the slurry and may be a cellulose derivative such as methyl-hydroxyethyl or sodium carboxymethyl cellulose; a polysaccharide gum or the like. Suitable anti-foaming agents may be added to inhibit excessive foaming during mixing. These would include silicones, petroleum solvents and phosphates, typical phosphates being iso octyl phosphate, triethyl phosphate, tri octyl phosphate or tri-N-butyl phosphate. The mildewcides may be added to prevent undesirable bacterial growth during extended storage and may include phenols such as pentachlorophenol, 2,4,5-trichlorophenol 2, 3,4,6 tetrachlorophenol or the like; or mercurials such as phenol mercury oleate, phenyl mercury acetate and the like.

The above mentioned reagents are illustrative only of the kinds of dispersing agents, thickening agents, defoamers and mildewcides that have been used successfully in producing the high-solids of this invention but it will be understood that the invention is not limited to these particular reagents but is comprehensive of others as enumerated in the preferred embodiment of the invention which follows.

10 The  $TiO_2$  pigments used in the slurries of this invention are especially designed to be used in paper and emulsion paints and to this end are rutile pigments having a post calcination treatment with the hydrous oxides of titanium, silicon and aluminum.

To prepare the slurries the aforesaid reagents are added to a medium such as water and thoroughly mixed after which the  $TiO_2$  pigment is added accompanied by vigorous agitation as for example by use of a high speed impeller mill.

20 The dispersants are used to insure good dispersion of the  $TiO_2$  pigment and as pointed out above are selected from a group of di-polar compounds having a high molecular weight, typical dispersants useful in preparing the high-solids slurries of this invention being polyphosphates such as potassium tripolyphosphate, tetrapotassium pyrophosphate and sodium hexametaphosphate. Other dispersants include the amines such as triethanolamine (TEA) and monoisopropanol-amine (MIPA), sodium salt of carboxylated poly-electrolyte, sodium citrate, sodium gluconate, ethylene oxide condensate (sodium or potassium salt), amino tris methyl phosphonic acid, methyl phosphonate, the sodium salt of condensed mono-naphthalene sulfonic acid, and the like.

30 The amount of dispersing agent or agents used in preparing the high-solids slurry of this invention is dependent on the amount and type of  $TiO_2$  pigment used as well as the nature of the dispersant itself i.e. whether it is a high or low active disper-

sant. It follows therefore that the dispersant level may vary considerably. In general the amount of dispersant used may vary from about 0.1% to as high as 5.0%, the higher percentages being used with low active dispersants. For all practical purposes however the amount of dispersant used will range from about 0.2% to 2.0% on a  $TiO_2$  basis.

10 The thickening agent is added to the slurry to reduce pigment settling and to maintain the desired viscosity characteristics essential to good rheology and pumpability. Suitable thickeners include water soluble hydroxy-groups containing organic colloids i.e. cellulose derivatives such as methyl hydroxethyl or sodium carboxymethyl cellulose, starches, polyvinyl alcohols or possibly alginates. Other thickeners that may be used include the "clay" types such as hydrous magnesium silicate or purified magnesium aluminum silicate; and also polysaccharide gum, sometimes referred to as xanthan gum, and certain acrylic type thickeners such as sodium polyacrylate, cross-linking acrylic copolymers and polyacrylic acid solutions.

These thickening agents are used in amounts which depend 20 upon the extent to which they are to influence settling and viscosity. In practice these amounts may vary from 0.0% to as high as 5% but for most applications the amounts used would range from 0.005% to 0.5% on a  $TiO_2$  weight basis.

To form an aqueous high solids slurry of uniformly dispersed  $TiO_2$  pigment it is important that the mixture be stirred vigorously. This frequently causes an excessive build-up of foam or air bubbles which is undesirable in a plant scale operation and hence defoaming or anti-foaming agents are sometimes added to minimize foaming. These agents may comprise the silicones, petroleum 30 solvents and phosphate types such as iso octyl phosphate, tri ethyl phosphate, tri octyl phosphate and the like. Concentrations of these ingredients vary with their strength and type. Normally

these anti-foaming reagents would be used in amounts ranging from 0.005% to 0.5% on a  $TiO_2$  weight basis but amounts as low as 0.001% and as high as 1.0% may be used.

The mildewcide is added to prevent biological degradation of the thickening agents and to inhibit bacterial growth and subsequent putrefaction of the aqueous slurries - especially when the slurry is to be stored over long periods of time. Suitable mildewcides are the phenol types such as pentachlorophenol, sodium salt, mono hydrate; 0-phenyl-phenol; 2,3,4,6 tetra chlorophenol and mercurials such as phenyl mercury 2-ethylhexylmaleate, phenyl mercury oleate, phenyl mercury acetate, phenyl mercuric propionate and the like. These materials may be added in amount ranging from 0.01% to 0.5% and on a  $TiO_2$  weight basis.

10 The invention is further illustrated by the following examples:

#### EXAMPLE 1

A predispersed aqueous rutile  $TiO_2$  pigment slurry at 70% solids by weight was prepared as follows:

20 To 574.8 grams water were added in the order named 0.4 grams of a purified magnesium aluminum silicate as thickener, 14.4 grams potassium tripolyphosphate as dispersant, 6.4 grams of sodium salt of carboxylated polyelectrolyte which also served as a dispersant, 2.0 grams of a silicone type defoamer and 2.0 grams of di(phenylmercury) dodecanyl succinate (10% Hg) which served as a mildewcide. The reagents and water were thoroughly mixed after which 1400.00 grams rutile latex grade  $TiO_2$  pigment were added and dispersed in the aqueous mixture by using a high speed impeller mill to form a homogeneous  $TiO_2$  pigment slurry of 70% solids by weight. Foaming was minimal during mixing and the slurry remained 30 in a uniformly dispersed pumpable condition after storage for a period of 140 days.

EXAMPLE II

A relatively low solids (64%) aqueous  $TiO_2$  slurry was prepared as follows:

To 711.3 grams of water were added in the order named 8.6 grams sodium gluconate as dispersant, 0.1% xanthan gum as thickener and 1280 grams of a rutile latex grade  $TiO_2$  pigment. The ingredients of the slurry were admixed as described in Example I and the final slurry was homogeneous and retained its uniformity and pumpability after 30 days storage.

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EXAMPLE III

As a further illustration of the invention a relatively high solids (77%)  $TiO_2$  slurry was prepared using an organic solvent as the liquid medium.

To 376.8 grams propylene glycol were added in the order named 11.2 grams of a silicone which served as a defoamer, 62.0 grams sodium salt of carboxylated polyelectrolyte as dispersant and 1550.0 grams rutile  $TiO_2$  pigment.

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The ingredients were mixed as described in Example I and the final slurry was homogeneous and had suitable viscosity for handling purposes even after 60 days of storage.

EXAMPLE IV

The scope of the invention is further illustrated by an example in which the liquid medium was a mixture of water and an organic solvent. Thus to 308.2 grams water and 92.4 grams ethylene glycol was added 9.2 grams potassium tripolyphosphate and 24.6 grams alkylphenoxy poly (oxyethylene) ethanol as dispersing agents, 18.4 grams tri-octyl phosphate as defoamer and 6.2 grams di(phenyl-mercury) dodecenyl succinate (10% Hg) as a mildewcide. To the above was added and dispersed, 1541.0 grams of titanium pigment.

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This slurry also had acceptable rheology after 30 days of storage.

While this invention has been described and illustrated by

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the examples shown, it is not intended to be strictly limited here-  
to, and other variations and modifications may be employed within  
the scope of the following claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

1. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment, said slurry comprising: a liquid medium selected from the group consisting of water, an organic solvent and mixtures thereof, from 60 to 80%  $TiO_2$  pigment, an organic dispersing agent in an amount in the range of from 0.1% to 5.0% and an organic thickening agent in an amount from 0.0% to 5.0%
2. As a new product of manufacture a pumpable high solids slurry of uniformly dispersed  $TiO_2$  pigment according to Claim 1 wherein said slurry includes an organic defoamer in an amount from 0.005 to 0.5%.
3. As a new product of manufacture a pumpable high solids slurry of uniformly dispersed  $TiO_2$  pigment according to Claim 1 wherein said slurry includes a mildewcide in an amount from 0.01 to 0.5%.
4. As a new product of manufacture a pumpable high solids slurry of uniformly dispersed  $TiO_2$  pigment according to Claim 1 wherein said slurry includes an organic defoamer and a mildewcide, said organic defoamer being present in an amount from 0.005 to 0.5% and said mildewcide present in an amount from 0.01 to 0.5%.
5. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment according to Claim 1 wherein the liquid medium is water.
6. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment according to any of claims 1, 2 or 3 wherein the liquid medium is a glycol selected from the group consisting of propylene and ethylene.
7. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment according to

any of claims 1, 2 or 3 wherein said dispersing agent is selected from the group consisting of potassium tripolyphosphate, sodium gluconate, sodium salt of carboxylated polyelectrolyte and alkyl-phenoxy poly (oxyethylene) ethanol.

8. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment according to any of claims 1, 2 or 3 wherein said thickening agent is selected from the group consisting of magnesium aluminum sulfate and xanthan gum.

9. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment according to any of claims 1, 2 or 3 wherein said defoamer is selected from the group consisting of silicone and tri octyl phosphate.

10. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment according to claim 5 wherein said dispersing agent comprises sodium gluconate and said thickening agent is xanthan gum.

11. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment said slurry comprising a homogeneous mixture of; 376.8 grams propylene glycol, 1550 grams  $TiO_2$ , 11.2 grams silicone as defoamer and 62.0 grams sodium salt of carboxylated polyelectrolyte as dispersant.

12. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment said slurry comprising: an aqueous homogeneous mixture of 711.3 grams water, 8.6 grams sodium gluconate as dispersant, 0.1 grams xanthan gum as thickener and 1280 grams of  $TiO_2$  pigment.

13. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment said slurry comprising; an aqueous homogeneous mixture of 574.8 grams of  $H_2O$ , 1440 grams  $TiO_2$  pigment, organic dispersing agents consisting of 14.4 grams potassium tripolyphosphate and 6.4 grams sodium salt of carboxylated polyelectrolyte, an organic thickening agent consisting of 0.4 grams magnesium aluminum silicate, 2.0

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grams silicone as defoamer and 2.0 grams di(phenylmercury) dodeceny succinate (10% Hg) as mildewcide.

14. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed  $TiO_2$  pigment said slurry comprising: an aqueous homogeneous mixture of 308.2 grams water, 92.4 grams ethylene glycol, organic dispersing agents consisting of 9.2 grams potassium tripolyphosphate and 24.4 grams alkylphenoxy poly (oxethylene) ethanol, a defoamer consisting of 18.4 grams tri octyl phosphate and moldewcide consisting of 6.2 grams di(phenylmercury) dodeceny succinate (10% Hg) and 1541.0 grams  $TiO_2$  pigment.



ABSTRACT OF THE DISCLOSURE

A pumpable, titanium dioxide pigment slurry from 50 to 80% solids is prepared by adding a thickening agent, a dispersant, and optionally a defoamer and a mildewcide to a liquid medium, mixing the reactants thoroughly to insure homogeneity and then adding  $TiO_2$  pigment which is dispersed by a high speed dispersator.

EXHIBIT

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US005527853A

**United States Patent** [19]

Landy et al.

[11] **Patent Number:** 5,527,853[45] **Date of Patent:** Jun. 18, 1996[54] **SHELF STABLE FAST-CURE AQUEOUS COATING**

[75] Inventors: Frank Landy, Jenkintown; Andrew Mercurio, Gwynedd Valley; Roy Flynn, Warrington, all of Pa.

[73] Assignee: Rohm and Haas Company, Philadelphia, Pa.

[21] Appl. No.: 340,461

[22] Filed: Nov. 14, 1994

**Related U.S. Application Data**

[63] Continuation of Ser. No. 32,735, Mar. 15, 1993, abandoned, which is a continuation of Ser. No. 879,542, May 4, 1992, abandoned, which is a continuation of Ser. No. 383,944, Jul. 21, 1989, abandoned.

[51] Int. Cl. <sup>6</sup> C08K 5/35

[52] U.S. Cl. 524/521; 524/314

[58] Field of Search 524/521, 314, 524/96, 247, 249; 526/312, 308, 310

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*Primary Examiner*—Jeffrey T. Smith  
*Attorney, Agent, or Firm*—Sudhir G. Deshmukh

## [57]

**ABSTRACT**

A shelf-stable fast-cure aqueous coating is disclosed. The coating contains an anionically stabilized latex, a polyfunctional amine and a volatile base in an amount sufficient to deprotonate the conjugate acid of the amine.

**19 Claims, No Drawings**

## SHELF STABLE FAST-CURE AQUEOUS COATING

This application is a continuation of U.S. application Ser. No. 08/032,735 filed Mar. 15, 1993, now abandoned which is a continuation, of application Ser. No. 879,542, filed May 4, 1992, now abandoned, which is a continuation, of application Ser. No. 383,944, filed Jul. 21, 1989, now abandoned,

### BACKGROUND OF THE INVENTION

This invention relates to aqueous coatings, particularly aqueous road-marking paint that dries quickly after application.

Various attempts to produce an aqueous road-marking paint as a substitute for solvent-based road marking paints have been disclosed in the art. A significant problem has been that the aqueous paints do not dry quickly enough.

European Patent Application No. 200249 discloses applying an aqueous dispersion of polymer to the road and then contacting the composition with a water soluble salt to cause the coating to dry rapidly and resist washout by a rain shower five minutes after application. This disclosure would require spraying with two compositions which would require the use of extra equipment.

European Patent application 0 066 108 discloses an aqueous road marking composition in which the binder is a mixture of a pure acrylic resin, a carboxylated styrene/dibutyl fumarate copolymer and a polymeric, polyfunctional amine such as polypropylenimine. This application states that the disclosed compositions are not storage stable beyond 48 hours after which more polyfunctional amine must be added to restore activity.

### SUMMARY OF THE INVENTION

The present invention provides a coating composition that dries quickly, develops water resistance soon after application and retains reactivity after storage.

The aqueous coating composition contains anionically stabilized emulsion polymer having a Tg greater than about 0° C., an effective amount of polyfunctional amine and a volatile base in an amount effective to raise the pH of the composition to a point high enough for the polyfunctional amine to be essentially in a non-ionized state (deprotonation) thereby eliminating polyamine interaction with the anionically stabilized emulsion and anionic ingredients in the coating.

In one aspect the invention provides an aqueous road or pavement-marking paint. The aqueous road or pavement marking paint of the invention can be used to mark lines or symbols on roads, parking lots walkways, etc. of various compositions such as asphaltic, bituminous or concrete paving with or without aggregate filler or top-dressing. This aqueous road-marking paint dries quickly, to develop early resistance to washout and tire tread printing.

### DETAILED DESCRIPTION OF THE INVENTION

The aqueous coating composition is made from:

- (A) an anionically stabilized polymer latex;
- (B) a soluble or dispersible, preferably a soluble, polymer produced from monomer units in which from about 20% to 100% by weight of the monomer units contain an amine group;

(C) a volatile base in an amount effective to raise the pH of the composition to a point high enough for the polyfunctional amine to be essentially in a non-ionized state (deprotonation) thereby eliminating polyamine interaction with the anionically stabilized emulsion and anionic ingredients in the coating. The volatile base must be volatile enough to be released under air dry conditions.

### Anionically Stabilized Polymer

The anionically stabilized emulsion polymer can be prepared by known procedures, which are published in texts on the subject such as "Emulsion Polymerization: Theory and Practice" by D. C. Blackley published by Wiley in 1975 and "Emulsion Polymerization" by F. A. Bovey et al. published by Interscience Publishers in 1965. In general, the anionically stabilized latex polymer is a polymer or copolymer prepared from monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, styrene, butadiene, ethylene, vinyl acetate, vinyl ester of "Versatic" acid (a tertiary monocarboxylic acid having C<sub>9</sub>, C<sub>10</sub> and C<sub>11</sub> chain length, the vinyl ester is also known as "vinyl versatate"), vinyl chloride, vinyl pyridine, vinylidene chloride, acrylonitrile, chloroprene, acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid. Polymers and copolymers of alpha-beta ethylenically unsaturated monomers and their esters, especially the acrylic and methacrylic esters, are preferred and are preferably prepared by processes given in "Emulsion Polymerization of Acrylic Monomers: May, 1966" published by the Rohm and Haas Company, Philadelphia, Pa., incorporated herein by reference.

The negative charge on the dispersed latex particles is obtained in any of several ways, the most common being the use of anionic surfactants or dispersants as the stabilizer during the emulsion polymerization or added to the emulsion after polymerization. Nonionic surfactants may, of course, also be present in the latex during or after polymerization of these anionically stabilized latexes. Among the useful surfactants and dispersants are the salts of fatty rosin and naphthenic acids, condensation products of naphthalene sulfonic acid and formaldehyde of low molecular weight, carboxylic polymers and copolymers of the appropriate hydrophilic-lipophile balance, higher alkyl sulfates, such as sodium lauryl sulfate, alkyl aryl sulfonates, such as dodecylbenzene sulfonate, sodium or potassium isopropylbenzene sulfonates or isopropylnaphthalene sulfonates; sulfosuccinates, such as sodium dioctylsulfosuccinate alkali metal higher alkyl sulfosuccinates, e.g. sodium octyl sulfosuccinate, sodium N-methyl-N-palmitoyltaurate, sodium oleyl isethionate, alkali metal salts of alkylarylpolyethoxyethanol sulfates or sulfonates, e.g. sodium t-octylphenoxy-polyethoxyethyl sulfate having 1 to 5 oxyethylene units, and the various other anionic surfactants and dispersants well-known in the art.

Another type of negatively-charged latex is that which is obtained as a result of including in the polymers small amounts of acidic groups, which may be in the salt form, such as an alkali metal or ammonium salt. Examples of such acidic groups are those derived from incorporated initiator fragments, maleic acid, vinyl sulfonic acid, crotonic acid, acrylic acid, methacrylic acid, itaconic acid, and the like.

The polymer must have a glass transition temperature (Tg) above 0° C. Polymers having a Tg below 0° C. are generally not useful since they are too soft, resulting in poor

scrub resistance and accelerated dirt pickup. The invention may also be practiced using polymers of more complex morphology, such as core-shell particles. These complex polymer morphologies usually display multiple Tg's and may display a Tg value below 0 degrees C. as one of its multiple Tg's, however the average or effective Tg of the polymer must be above about 0 degrees C.

To prepare a storage stable composition of the amine-containing polymer and the anionically stabilized emulsion polymer, the amine-functional polymer is maintained essentially in a nonionic state by adding a sufficient amount of volatile base to raise the pH of the composition at or near the point at which substantially all the amine functional groups are in a nonionic state (deprotonation) and therefore do not interact with the anionically stabilized latex. A starting point estimate of the amount of volatile base required to reach this point can be calculated from the number of equivalents of base needed to neutralize all of the acid groups in the latex (i.e. acid groups from: copolymerized carboxylic-bearing monomer; surfactant; or initiator) and the conjugate acid of the amine base. If the amine is not sufficiently deprotonated, the emulsion will exhibit observable signs of instability over time, such as viscosity increase and microscopically observable "particle rafting", an early stage of aggregation/gellation. One equivalent of volatile base (based on latex acids and polyamine titers) is usually enough to yield a stable system although higher levels of volatile base (-3 to 4 equivalents) may be necessary for long term stability. Higher amounts of volatile base can be used without departing from the spirit of the invention although the "quick dry" properties of the coating may be reduced. If the equipment used in the process of manufacture presents opportunities for loss of the volatile base by evaporation at any stage from when the volatile base is added until after the product is packaged in a sealed container, the amount of volatile amine loaded to the production equipment should be increased to offset the loss.

After application, the volatile base evaporates thus lowering the pH of the composition. When the pH of the composition falls to a point where the protonation of the polyamine begins to occur, the polyamine becomes cationic. The quick dry is believed to be initiated by this conversion of the polyamine to a cationic polymer in the presence of the anionically stabilized emulsion polymer, although the exact mechanism that produces the quick-dry property has not been established.

#### Polyfunctional Amine

The compositions of this invention contain a polyfunctional amine, preferably a polymer containing from about 20% to 100%, and preferably at least 50% by weight of amine-containing monomer. Examples of the amine containing monomers include members of the following classes:

#### Amine Classes

1. Aminoalkyl vinyl ethers or sulfides wherein the alkyl groups may be straight-chain or branched-chain type and have from two to three carbon atoms and wherein the nitrogen atom may be a primary, secondary, or tertiary nitrogen atom (U.S. Pat. No. 2,879,178). In the latter instance, one of the remaining hydrogen atoms may be substituted by alkyl, hydroxyalkyl, or alkoxyalkyl groups, the alkyl components of which may have one to four carbon atoms, preferably one carbon atom only. Specific examples include:

beta-aminoethyl vinyl ether; beta-aminoethyl vinyl sulfide; N-monomethyl-beta-aminoethyl vinyl ether or sulfide; N-monoethyl- beta -aminoethyl vinyl ether or sulfide; N-monobutyl- beta -aminoethyl vinyl ether or sulfide; and N-monomethyl-3-aminopropyl vinyl ether or sulfide.

2. Acrylamide or acrylic esters, such as those of the formula II:



wherein

R is H or CH<sub>3</sub>;

n is 0 or 1;

X is O or N(H);

When n is zero, A is O(CH<sub>2</sub>)<sub>x</sub>, wherein x is 2 to 3, or (O-alkylene), wherein (O-alkylene), is a poly(oxyalkylene) group, having a molecular weight in the range from 88 to 348, in which the individual alkylene radicals are the same or different and are either ethylene or propylene; and

when n is 1, A is an alkylene group having two to 4 carbon atoms;

R\* is H, methyl, or ethyl; and

R<sup>1</sup> is H, methyl, or ethyl; and

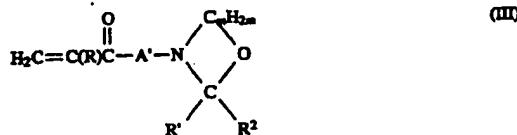
R<sup>0</sup> is H, phenyl, benzyl, methylbenzyl, cyclohexyl, or (C<sub>1</sub>-C<sub>6</sub>) alkyl.

Examples of compounds of formula II include:

dimethylaminoethylacrylate or methacrylate; beta -aminoethyl acrylate or methacrylate; N- beta -aminoethyl acrylamide or methacrylamide; N-(monomethylaminoethyl)-acrylamide or methacrylamide; N-(mono-n-butyl)-4-aminobutyl acrylate or methacrylate; methacryloyloxyethylamine; and

acryloyloxypropoxypropoxypropylamine.

3. N-acryloxyalkyl oxazolidines and N-acryloxyalkyl tetrahydro-1,3-oxazines and the corresponding compounds in which the "alkyl" linkage is replaced by alkoxyalkyl and poly(alkoxy-alkyl), all of which are embraced by Formula III:



wherein

R is H or CH<sub>3</sub>;

m is an integer having a value of 2 to 3;

R', when not directly joined to R<sup>2</sup>, is selected from the group consisting of hydrogen, phenyl, benzyl, and (C<sub>1</sub>-C<sub>12</sub>) alkyl groups;

R<sup>2</sup>, when not directly joined to R', is selected from the group consisting of hydrogen and (C<sub>1</sub>-C<sub>4</sub>) alkyl groups;

R' and R<sup>2</sup>, when directly joined together, form a 5- to 6-carbon ring with the attached carbon atom of the ring in the formula, i.e., R' and R<sup>2</sup>, when joined together, are selected from the group consisting of pentamethylene and tetramethylene; and

A' is O(C<sub>m</sub>H<sub>2m</sub>)<sub>n</sub> or (O-alkylene)<sub>n</sub>, in which (O-alkylene)<sub>n</sub>, is a poly(oxyalkylene) group, having a molecular weight in the range from 88 to 348, in which the individual alkylene radicals are the same or different and are either ethylene or propylene.

The compounds of Formula III can hydrolyze under various conditions to secondary amines. The hydrolysis produces products having the Formula IV:



to small extent of hydrolysis during synthesis, storage or use.

#### Volatile Base

The type and amount of volatile base used must be sufficient to raise the pH of the composition to about the point where the polyfunctional amine is non-ionized (deprotonated), to avoid interaction with the anionically stabilized emulsion. The volatile base of preference is ammonia, which may be used as the sole volatile base or in admixture with other volatile or nonvolatile bases. Other volatile bases which may be employed are morpholine, the lower alkyl amines, 2-dimethylaminoethanol, N-methylmorpholine, ethylenediamine, and others.

Filler, extenders, pigments and other additives known in the art may also be used in the compositions of the invention. If pigment is used in the traffic paint composition, it is typically in the range of fifty percent pigment volume content to sixty percent pigment volume content. Examples of pigments that may be employed include clays, calcium carbonate, talc, titanium dioxide, carbon black, and various colored pigments.

Care must be exercised when selecting the type and amount of additives to avoid altering the pH of the composition to an extent that interferes with storage stability or buffering the pH to an extent that after application the pH does not fall sufficiently to initiate protonation of the polyamine. For example a paint prepared using a polyamine with a relatively low pKa and too large an amount of calcium carbonate as filler, may display an unacceptably extended cure time.

Traffic paint compositions typically have a solids content in the range of from thirty-five% to seventy% by volume and a viscosity of from about 70 kreb units to about 100 kreb units. Coatings provided by the invention are also useful in other exterior coatings such as maintenance coatings, house paint, etc..

The following examples illustrate some aspects of the invention and should not be construed as limiting the scope of the invention which is described in the specification and claims.

#### Abbreviations:

AM=Acrylamide

DMAEMA=Dimethylaminoethylmethacrylate

DMAPMA=Dimethylaminopropylmethacrylamide

HEMA=Hydroxyethylmethacrylate

MMA=Methylmethacrylate

OXEMA=Oxazolidinoethylmethacrylate

p-OXEMA=poly-oxazolidinoethylmethacrylate

#### Paint Preparation

The test paints were prepared according to the following standard paint formulation by grinding together the ingredients listed as grind ingredients below and then adding the remaining ingredients in the letdown. The emulsion was an anionic copolymer of butyl acrylate, methyl methacrylate and methacrylic acid having a  $T_g$  of 20° C., and a particle size of 200 nanometers.

Grind Ingredient	Amount (lbs/103 gals)
Emulsion (50% solids)	457.9
Water	28.4

-continued

Grind Ingredient	Amount (lbs/103 gals)
Tamol 850	7.1
Triton CF-10	2.8
Drew L-493	1.0
TPure R900	100.0
Silverbond B	156.3
Snowflake-(calcium carbonate)	595.9
<u>LetDown</u>	
Texanol	22.9
Methanol	15.0
Drew L-493	2.0
Hydroxyethyl cellulose 250 MR (2.5% solution in water)	15.0
	1,404.3

#### DESCRIPTION OF TEST METHODS

##### Dry Time Test

This test is similar to ASTM D1640 which is a standard test for drying of organic coatings at room temperature. The test films are applied on a non-porous substrate (glass plate or metal panel) by suitable means to give a wet film thickness of 0.012+/-0.001 inches. The ASTM test method is modified in that only minimal thumb pressure is used. The thumb is turned through an angle of 90° while in contact with the film. The drying time at which this rotation does not break the film is recorded.

##### Early Washout Resistance

The test films are prepared in the same manner as for the dry time test. After the films have dried for 15 minutes at a temperature of 78° F and 50% relative humidity, the samples were held under a stream of cold running water (tap pressure of 170-200 gallons per hour), which contacted the surface of the paint film at from a nearly perpendicular to an oblique angle. The samples remained under the stream of running water for a period of five (5) minutes. At the end of this period the samples were removed from the test stream and rated by visual inspection. Samples that showed no apparent effect were rated passes; those that exhibited slight disruption of the film were rated marginal; those samples that showed a break in the film or any film removal were rated as fails.

##### Scrub Resistance

Films of 3.5 mils dry thickness were prepared and cured for 24 hours at 77° F. +/- 2° F. and 40-55% relative humidity. The films were tested according to according to ASTM D2486. The number of scrub cycles at which to an area of the paint film was fully removed was recorded.

##### Heat Aging Test

One pint of the test paint was placed in a sealed can and stored in a sealed circulation oven at 120° F. for one week. The can was removed from the oven and the paint was observed. If the paint is still fluid and shows no apparent signs of bodying or separation it is rated as a pass.

9  
EXAMPLES

Comparative Example A—Addition of Polyamine to Anionic Polymer Latex Produces Paint That Is Not Storage Stable

To a paint formulation prepared according to the formulation described above, 10 lbs. of polyOXEMA (28.5% solids) was added. The consistency of this paint changed from a fluid mixture to a solidified mass on aging 16 hours at ambient temperature.

Example 1—Addition of Volatile Base Produces Paint That Is Storage Stable

The procedure of the Comparative Example was repeated except that 3.9 lbs. of ammonium hydroxide (28%) was added before the polyOXEMA. The paint remained fluid when stored at room temperature and passed the heat aging test.

Example 2—Various Levels of Polyamine

Test paints were prepared by adding polyamine (polyOXEMA), as in Example 1, in the amount indicated in the table as a percent by weight based on vehicle solids. The paints were applied to substrates and tested. The standard paint without any amine-containing polymer was used as a control. The results appear in the table below:

Level of Polyamine (% solids on vehicle solids)	Easy Washout Resistance	Scrub Resistance Properties
Control	fail	950 cycles
0.27% p.OXEMA	margin	
0.62% p.OXEMA	passes	760 cycles
1.25% p.OXEMA	passes	930 cycles
2.5% p.OXEMA	passes	910 cycles

The above data demonstrates that the amine-functional polymer produces early washout resistance with acceptable scrub resistance properties. Also, the paint containing 1.25% polyOXEMA dried in 10 minutes in the dry time test compared to 20 minutes dry time for the Control paint that doesn't contain polyamine.

Example 3—Use of Polymers and Copolymers of Various Amine-containing Monomers Demonstrated

Paints were prepared using the indicated amine-containing polymer according to the procedure of Example 1. The paint without any amine-containing polymer was used as a control. Samples were prepared by adding amine-containing polymer to the standard formulation in the amount indicated in the table measured as a percent by weight based on vehicle solids. The sample emulsions were applied to substrates and tested. The results appear in the table below:

Type of Polyamine in marking paint Formulation (1.25% S/S)	Early Washout Resistance	7 days aging 120° F.
none	fail	passes
pOXEMA	passes	passes
OXEMA/HEMA 50/50	passes	passes
OXEMA/MMA 70/30	passes	passes
DMAPMA/AM 70/30	passes	passes
DMAPMA/HEMA 70/30 (0.44% v/v)	passes	passes

10  
-continued

Type of Polyamine in marking paint Formulation (1.25% S/S)	Early Washout Resistance	7 days aging 120° F.
pDMAEMA	passes	passes

The above data demonstrates that marking paints according to the invention have early washout resistance and were storage stable even under storage at elevated temperature.

We claim:

1. A shelf-stable fast-cure aqueous coating composition consisting essentially of:

(a) an anionically stabilized emulsion polymer having a Tg greater than about 0° C.;

(b) a water soluble polyfunctional amine polymer having from about 20% to about 100% of the monomer units by weight containing an amine group and having no acid groups other than trace amounts; and

(c) an amount of volatile base sufficient to raise the pH of the composition to a point where essentially all of the polyfunctional amine is in a non-ionic state.

2. The composition of claim 1 wherein the amount of polyfunctional amine is from about 0.25 to about 10 parts per 100 parts emulsion solids by weight.

3. The composition of claim 2 wherein the amount of polyfunctional amine is from about 0.4 to about 5 parts per 100 parts emulsion solids by weight.

4. The composition of claim 3 wherein the amount of polyfunctional amine is from about 0.6 to about 2.5 parts per 100 parts emulsion solids by weight.

5. The coming composition of claim 1 wherein the polyfunctional amine is polyoxazolidinoethylmethacrylate.

6. The coating composition of claim 1 wherein the polyfunctional amine polymer contains dimethylaminoethylmethacrylamide.

7. The coming composition of claim 1 wherein the polyfunctional amine polymer contains oxazolidinoethylmethacrylate.

8. The coating composition of claim 1 wherein the polyfunctional amine polymer contains dimethylaminoethylmethacrylate.

9. A shelf stable fast-cure aqueous traffic paint consisting essentially of:

(a) an anionically stabilized emulsion polymer having a Tg greater than about 0° C.;

(b) a water soluble polyfunctional amine polymer; and

(c) an amount of volatile base sufficient to raise the pH of the composition to a point where essentially all of the polyfunctional amine is in a non-ionic state.

10. A shelf stable fast-cure aqueous paint composition consisting essentially of:

(a) an anionically stabilized emulsion polymer having a Tg greater than about 0° C.;

(b) a water soluble polyfunctional amine; and

(c) an amount of a volatile base sufficient to raise the pH of the composition to a point where essentially all of said polyfunctional amine is in a non-ionic state.

11. The composition of claim 10 wherein said polyfunctional amine is polymerized from 20% to 100% by weight of amine containing monomer units.

12. The composition of claim 11 wherein said monomer units are selected from the group consisting of dimethylaminoethylmethacrylamide, oxazolidinoethylmethacrylate and dimethylaminoethylmethacrylate.

13. An exterior shelf-stable fast-cure aqueous paint composition consisting essentially of:

- (a) an anionically stabilized emulsion polymer having a Tg greater than about 0° C.;
- (b) 0.6 to 2.5 parts per 100 parts of emulsion solids by weight of a water soluble polyfunctional amine polymer having no acid groups other than trace amounts and polymerized from oxazolidinoethylmethacrylate monomer units; and
- (c) an amount of a volatile base sufficient to raise the pH of the composition to a point where essentially all of said polyfunctional amine is in a non-ionic state. 10

14. A shelf stable fast-cure aqueous traffic paint composition consisting essentially of:

- (a) an anionically stabilized emulsion polymer having a Tg greater than about 0° C.;
- (b) a water soluble polyfunctional amine; and 15
- (c) an amount of a volatile base sufficient to raise the pH of the composition to a point where essentially all of said polyfunctional amine is in a non-ionic state.

15. The composition of claim 14 wherein said polyfunctional amine is polymerized from 20% to 100% by weight of 20 amine containing monomer units.

16. The composition of claim 15 wherein said monomer units are selected from the group consisting of dimethylaminoethylmethacrylamide, oxazolidinoethylmethacrylate and dimethylaminoethylmethacrylate.

17. An exterior shelf-stable fast-cure aqueous traffic paint composition consisting essentially of:

- (a) an anionically stabilized emulsion polymer having a Tg greater than about 0° C.;
- (b) 0.6 to 2.5 parts per 100 parts of emulsion solids by weight of a water soluble polyfunctional amine polymer polymerized from oxazolidinoethylmethacrylate monomer units; and
- (c) an amount of a volatile base sufficient to raise the pH of the composition to a point where essentially all of said polyfunctional amine is in a non-ionic state. 15

18. The composition of claim 17 wherein said emulsion polymer has a Tg of 20° C.

19. The composition of claim 17 wherein the amount of said polyfunctional amine is 1.25 parts per 100 parts of emulsion solids.

\* \* \* \* \*

EXHIBIT

20

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## United States Patent [19]

Tsuei

[11] Patent Number: 5,643,669

[45] Date of Patent: Jul. 1, 1997

[54] CURABLE WATER-BASED COATING COMPOSITIONS AND CURED PRODUCTS THEREOF

[75] Inventor: Alexander C. Tsuei, Woodbury, Minn.

[73] Assignee: Minnesota Mining and Manufacturing Company, St. Paul, Minn.

[21] Appl. No.: 598,491

[22] Filed: Feb. 8, 1996

[51] Int. Cl. 6 C09K 3/14; B32B 27/06; C08K 5/06

[52] U.S. Cl. 428/354; 428/483; 428/908.8; 524/376; 524/377; 51/298

[58] Field of Search 428/355, 354, 428/328, 329, 483, 516, 908.8, 323; 524/376, 377; 51/298

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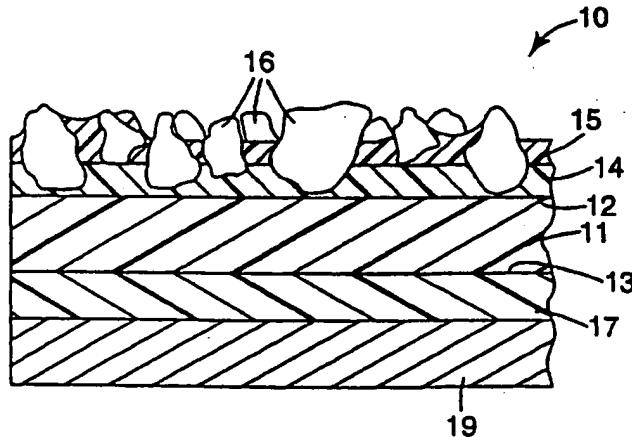
Primary Examiner: Daniel Zirker

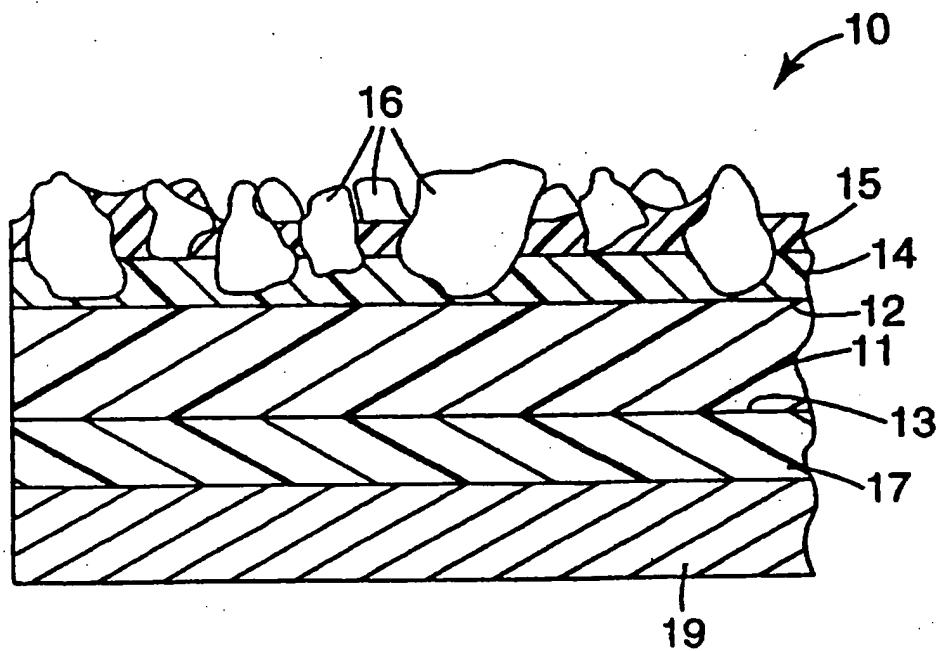
Attorney, Agent, or Firm: Gary L. Griswold; Walter N. Kinn; Daniel R. Pastur

## [57] ABSTRACT

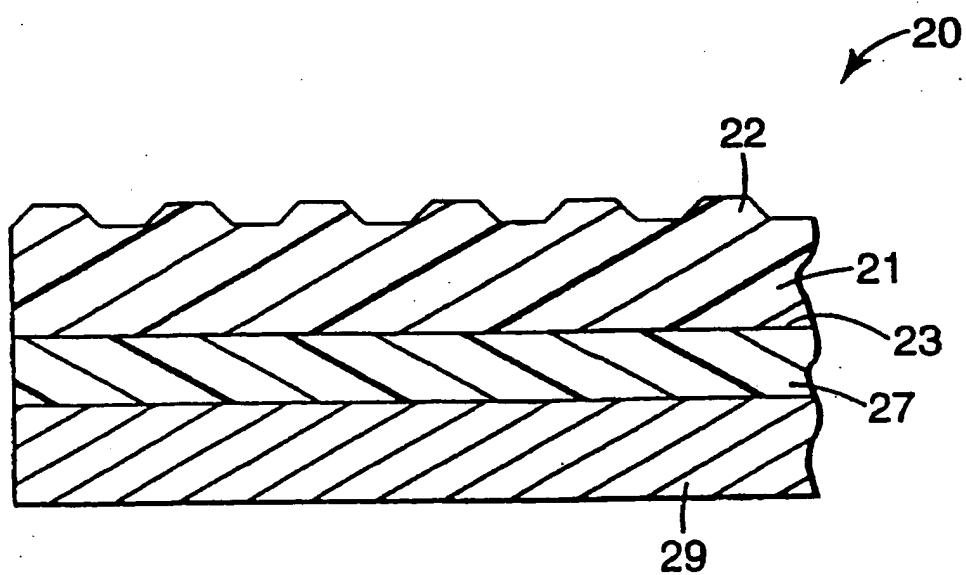
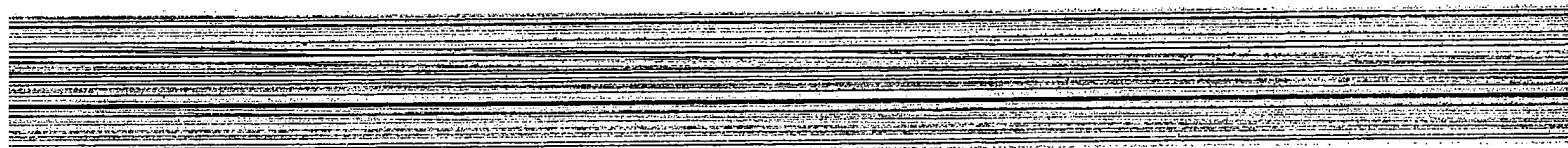
A low VOC curable water-based coating composition is provided. The composition includes a urethane/acrylic copolymer having a Tg of greater than about 50° C., a polyoxyethylene aryl ether plasticizer, an alkaline-stable crosslinker, and water, wherein the curable water-based coating composition includes less than about 5 wt-% volatile organic compounds, based on the total weight of the composition.

11 Claims, 1 Drawing Sheet





*Fig. 1*



*Fig. 2*

# CURABLE WATER-BASED COATING COMPOSITIONS AND CURED PRODUCTS THEREOF

## FIELD OF THE INVENTION

The present invention provides a curable water-based coating composition. Specifically, the present invention provides a curable water-based urethane/acrylic copolymer coating composition for use as a bond system in antislip products and abrasive articles, for example.

## BACKGROUND OF THE INVENTION

Water-based polymer dispersions are finding favor in many markets, not only because they provide performance similar to that obtained from conventional organic solvent-based products, but also because they are leading a worldwide movement toward the use of more environmentally friendly products. Generally, water-based polyurethane dispersions offer a variety of advantages, including ease-of-handling, nonflammability, and low toxicity, as well as premium performance. Thus, they are of interest for use in a wide variety of markets. It would be desirable to use them, for example, as make and/or size coatings for coated abrasive articles and antislip products (often referred to as friction surface sheet materials and nonskid sheet materials).

Typically, polyurethane dispersions are alkaline and stabilized such that the polyurethane particles do not agglomerate and/or settle out of the water. This can be done, for example, by neutralizing dispersed polymer acid moieties, such as pendant carboxylic acid moieties, with a basic compound such as ammonia or an amine, e.g., triethylamine. ~~Coatings prepared from many such dispersions generally require the addition of one or more coalescing agents, typically coalescent solvents or "cosolvents," to allow the formation of a useful film upon drying. Glycol ethers, such as alkyl ethers of ethylene or propylene glycol, have been successfully employed as cosolvents in such applications. However, the use of coalescing organic solvents in water-based systems increases the concentration of undesirable volatile organic compounds (VOCs).~~

Prior to the present invention, urethane/acrylic copolymers have been used in water-based curable coating compositions, but not without the use of undesirable amounts of a VOC coalescing agent. A "volatile organic compound" or "VOC," as used herein, is an organic compound that has a vapor pressure of at least 0.1 mm Hg at 20° C. Under this definition, ethylene glycol monobutyl ether (available from Union Carbide, Danbury, Conn., under the trade designation butyl "Cellosolve"), diethylene glycol monoethyl ether (available from Union Carbide under the trade designation "Carbitol"), propylene glycol n-butyl ether (available from ARCO Chemicals, Newtown Square, Pa., under the trade designation "Arcosolve" PNB), and dipropylene glycol n-butyl ether (available from ARCO Chemicals, under the trade designation "Arcosolve" DPNB), are considered VOCs. Furthermore, relatively large amounts (e.g., about 20% by weight (wt-%) or greater, based on polymer solids) of such coalescing agents have been typically required for effective film formation. Thus, it would be desirable to develop a coating composition for various applications, including for use as a bond material for the manufacture of abrasive articles and antislip products that contain low levels of VOCs.

## SUMMARY OF THE INVENTION

The present invention provides a curable water-based coating composition, the cured coating produced therefrom,

and articles including the cured coating such as antislip products and abrasive articles. The curable water-based coating composition includes: a urethane/acrylic copolymer having a Tg of greater than about 50° C.; a polyoxyethylene aryl ether plasticizer; an alkaline-stable crosslinker; and water; wherein the curable water-based coating composition includes less than about 5 wt-% volatile organic compounds, based on the total weight of the composition.

A preferred embodiment of the curable water-based coating composition includes: a urethane/acrylic copolymer having a Tg of greater than about 50° C.; a polyoxyethylene aryl ether plasticizer; a polyfunctional aziridine crosslinker; an associative thickener; a surfactant; and water; wherein the curable water-based coating composition includes less than about 5 wt-% volatile organic compounds, based on the total weight of the composition.

The present invention also provides articles, which can be antislip products or abrasive articles (e.g., coated abrasive products, bonded abrasive products, and nonwoven abrasive products), that include a cured binder prepared from the curable water-based coating composition of the invention. One embodiment of an antislip product may be prepared from a bond system comprising the curable water-based coating composition that includes: a urethane/acrylic copolymer having a Tg of greater than about 50° C.; a polyoxyethylene aryl ether plasticizer; an alkaline-stable crosslinker; and water; wherein the curable water-based coating composition includes less than about 5 wt-% volatile organic compounds, based on the total weight of the composition; and a multitude of frictional particles uniformly distributed therein in an amount which on curing provides a frictional surface.

The antislip products may be a sheet comprised of the cured binder/frictional particle composition in a free-standing sheet-like structure (i.e., a cured coating without a backing sheet), or it may be a coating on a backing, either of which may include on a surface opposite the friction surface a layer of pressure sensitive adhesive. In still another embodiment, the cured coating may have a frictional surface provided by an embossed surface, which may or may not include friction particles.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an enlarged cross-sectional view of a segment of an antislip sheet material of the present invention, which contains frictional particles.

FIG. 2 is an enlarged cross-sectional view of a segment of an alternative antislip sheet material of the present invention, which includes an embossed friction surface.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides curable water-based coating compositions that include urethane/acrylic copolymers having a glass transition temperature (Tg) of greater than about 50° C. The curable water-based coating compositions of the present invention do not include undesirable amounts of a VOC coalescing agent. Surprisingly, film formation is facilitated by the addition of polyoxyethylene aryl ether plasticizer, which is a nonfugitive (i.e., substantially nonvolatile) plasticizer, which dramatically diminishes organic emissions, particularly during the drying and curing process. Furthermore, such nonfugitive plasticizer is used in a relatively minor amount, preferably, in an amount of no greater than about 10 wt-%, and more preferably, no greater than about 5 wt-%, based on polymer solids.

Thus, curable water-based coating compositions of the present invention do not contain an undesirable amount of VOCs, preferably, they contain less than about 5 wt-%, and preferably less than about 2 wt-%, VOCs, such as coalescing solvents, based on the total weight of the composition (including water). The major VOC in the curable coating compositions of the present invention is typically triethylamine, which is often used to stabilize water-based dispersions of urethane-containing polymers. Other possible VOCs that may be included within the curable coating compositions of the present invention include, for example, dimethylethanol amine, isopropanol, and the like, typically, in small amounts to facilitate processing of the curable coating compositions of the present invention.

The low VOC curable water-based coating compositions of the present invention are aqueous polymer dispersions that can be used as the bond system or binder in antislip products or abrasive articles, or as protective coatings, paints, primers, edge sealers, etc. Preferably, the curable coating compositions of the present invention have a solids content of about 30-70 wt-%, more preferably, about 35-65 wt-%, based on the total weight of the composition (including the water). With a solids content of less than about 30 wt-%, the curable coating composition is generally too thin for most applications to form a useful cured coating, although it may be used in applications that require thin coatings. With a solids content of more than about 70 wt-%, the curable coating composition is generally too viscous to coat with conventional coating systems, although it may be extrusion coated or conventionally packaged for sale as a concentrate for dilution with water prior to use.

The low VOC curable water-based coating compositions of the present invention provide cured coatings that adhere well to a wide variety of materials, such as metals, plastics, etc. They provide not only protective coatings for substrates but good coating binders for holding frictional particles (e.g., minerals) to backing sheets, such as plastic films, in abrasive articles and antislip products, for example, with the process benefits of water-based products.

Preferably, cured coatings prepared from the low VOC curable water-based coating compositions of the present invention are durable, chemically resistant, and abrasion resistant. A durable cured coating preferably exhibits the ability to withstand at least about 4000 cycles on a flex fatigue resistance tester (flexed to 270° per cycle) with a 0.91 kg load, without cracking, and if coated on an aziridine-primed polyester film, without delaminating or losing more than about 5 wt-% frictional particles if they are included therein. A durable coating also preferably possesses a tensile strength when tested on a tensile strength testing device of at least about 530 kg/cm<sup>2</sup> at a crosshead speed of 30.5 cm/minute as a cured free-standing coating (i.e., a cured coating without a backing sheet). A chemically resistant cured coating preferably withstands immersion in a variety of inorganic and organic chemicals, such as 1% hydrochloric acid, isopropanol, methyl ethyl ketone, and water, for seven days without discoloration or haziness, delamination from an aziridine-primed polyester film, or loss of more than about 5 wt-% frictional particles if they are included therein. An abrasion resistant cured coating in the absence of frictional particles preferably loses no more than about 200 mg per sample after about 1000 cycles on a Taber Abraser abrasion testing device according to the test described in the examples.

The low VOC curable water-based coating compositions of the present invention include a urethane/acrylic copolymer having a Tg of greater than about 50° C., a polyoxy-

ethylene aryl ether plasticizer, and an alkaline-stable crosslinker. Optional additives include, for example, a thickener and a surfactant. In the absence of coalescing solvents, the urethane/acrylic copolymer dispersion does not typically form a polymer film. That is, the dispersed polymer particles without coalescing solvent do not meld during the drying and curing process. Although a thickener can aid in the formation of a polymer film from a water-based urethane/acrylic copolymer dispersion, such films are typically brittle, possibly due to poor coalescence, while the nonfugitive plasticizer aids in the formation of a coalesced, flexible film, such films tend to have a low tensile strength. For example, although a coating prepared only from a urethane/acrylic copolymer and about 2 wt-% of a polyoxyethylene aryl ether plasticizer, based on the total weight of the dispersion, forms a good film, it typically has a tensile strength of less than about 200 kg/cm<sup>2</sup>. The addition of an alkaline-stable crosslinker to the curable coating composition typically increases the tensile strength of a cured coating by about 300 kg/cm<sup>2</sup>, as compared to a cured coating prepared without an alkaline-stable crosslinker.

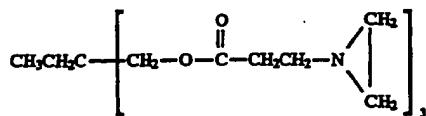
Suitable urethane/acrylic copolymers (i.e., a polymer containing urethane ( $-\text{R}^1\text{NHC(O)OR}^2-$ ) and acrylic  $-\text{R}^3-\text{C(O)OH}$  moieties) for use in the compositions of the present invention are those that are capable of forming stable dispersions in water and have a Tg of greater than about 50° C. Preferably, the urethane/acrylic copolymers are aliphatic urethane/acrylic copolymers with an acid number of about 15-16. Typically, stability is accomplished with the use of a stabilizer such as ammonia or triethylamine, for example, which interacts with the acid groups in the polymer. Urethane/acrylic copolymers having a Tg of greater than about 50° C. are typically nonfilm-forming polymers. As used herein, a "nonfilm-forming" polymer is one that is not capable of forming a film in the absence of a coalescing solvent, even at elevated temperatures. Such nonfilm-forming urethane/acrylic copolymers are commercially available. For example, a particularly preferred nonfilm-forming urethane/acrylic copolymer is a high solids, monomer-free, radiation-curable, water-borne urethane/acrylic copolymer, which is commercially available under the trade designation "NeoPac R-9699" from Zeneca Resins Inc., Wilmington, Mass. This urethane/acrylic copolymer is designed for high performance uses, where hardness, flexibility, UV resistance, chemical resistance, and abrasion resistance are desired. It has an acid number of 15. It is provided as a translucent dispersion containing 40 wt-% solids and having a Brookfield viscosity of 100 centipoise at 25° C. It is supplied with a VOC content of 1.1 wt-%, which results from the incorporation of triethylamine as a stabilizer. Prior to the present invention, it was believed that this material required the addition of a VOC coalescing solvent to form a good film.

The low VOC curable water-based coating compositions of the present invention use a polyoxyethylene aryl ether plasticizer as the coalescing agent for the nonfilm-forming urethane/acrylic copolymers. This nonfugitive plasticizer not only enhances film formation, but contributes to the flexibility of the coating. Because this plasticizer is not a VOC and does not significantly evaporate from the curable coating composition or cured coating, the present invention provides a significant advancement in the urethane/acrylic water-based coating art. Preferably, the plasticizers are polyoxyethylene aryl ether compounds of the general formula HO—(—CH<sub>2</sub>—CH<sub>2</sub>—O—)<sub>x</sub>—C<sub>6</sub>H<sub>5</sub>, wherein x=4-10, more preferably, x=4-6, and most preferably, x=4. Generally, as the chain length increases (i.e., with a larger

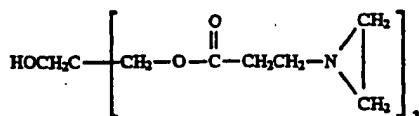
value of  $x$ ), the hydrophilicity of these compounds increases, and their performance decreases. For example, a cured coating made from a composition containing a plasticizer of the formula listed above with a value of  $x$  greater than 10 will typically exhibit poor flex fatigue resistance. Suitable polyoxyethylene aryl ether plasticizers are commercially available from ICI Americas, Inc., Wilmington, Del., under the trade designations "Pycal 94" ( $x=4$ ), "Hypermer 1L-2718" ( $x=6$ ), "Hypermer 1L2719" ( $x=8$ ), and "Hypermer 1L-2707" ( $x=10$ ). These plasticizers typically also function as wetting agents in the compositions of the present invention.

A polyoxyethylene aryl ether plasticizer, or mixture of such plasticizers, is present in the curable coating compositions of the present invention in an amount effective to meld the urethane/acrylic particles during the drydown or curing stage and thereby allow a continuous film to form. Preferably, a polyoxyethylene aryl ether plasticizer, or mixture of such plasticizers, is present in the curable coating compositions of the present invention in an amount of no greater than about 15 wt-%, based on the weight of polymer solids. More preferably, the curable coating compositions include about 1-10 wt-%, most preferably, about 3-6 wt-%, plasticizer, based on the weight of polymer solids. If more than about 15 wt-% of the plasticizer is used in the curable compositions of the present invention, relative to the weight of polymer solids, a tacky cured coating results that is not suitable for the present applications. As used herein, "polymer solids" refers to the weight of solids residue remaining after drydown of the principal polymers used in the composition. The "principal polymers" are those that are capable of crosslinking (e.g. urethane/acrylic copolymers, aliphatic urethanes, acrylic copolymers, and other polymers containing pendant carboxylic acid groups). This does not include adjunct components such as plasticizers, thickeners, and the like. This distinction is well known to one of skill in the art.

A crosslinker is included in the curable coating compositions of the present invention to enhance the tensile strength of the cured coating and improve its chemical resistance, for example. Suitable crosslinkers are those that can be used to crosslink urethane/acrylic copolymers and are stable in aqueous alkaline solutions. Examples of such crosslinkers include, but are not limited to, aziridine derivatives. Preferably, the crosslinker is a polyfunctional aziridine compound, and more preferably, a trifunctional aziridine compound. Suitable polyfunctional aziridines are those commercially available under the trade designations "XAMA-2" (trimethylolpropane-tris-( $\beta$ -(N-aziridinyl) propionate) of the following formula:



and "XAMA-7" (pentaerythritol-tris-( $\beta$ -(N-aziridinyl) propionate) of the following formula:



from B. F. Goodrich Chemical Co., Cleveland, Ohio, and "NeoCryl CX-100" from Zeneca Resins, Wilmington, Mass. These crosslinkers are particularly desirable because they

also function as adhesion promoters to materials such as polyesters, glass, etc. They are preferably used with polymers containing active hydrogens, such as the urethane/acrylic copolymers described above that contains pendant carboxylic acid groups.

An alkaline-stable crosslinker, or mixture of alkaline-stable crosslinkers, is present in the curable coating compositions of the present invention in an amount effective to provide a durable cured coating. Preferably, an alkaline-stable crosslinker, or mixture of alkaline-stable crosslinkers, is present in an amount effective to provide a cured coating with a tensile strength of at least about 530 kg/cm<sup>2</sup>. More preferably, an alkaline-stable crosslinker is present in the curable coating compositions of the present invention in an amount of about 2-8 wt-%, and more preferably, about 4-6 wt-%, based on the weight of polymer solids.

A thickener may be used in the curable coating compositions of the present invention to increase the viscosity of the dispersions. This is sometimes important to provide coatings that do not sag. Suitable thickeners are those that are compatible with urethane/acrylic dispersions. As used herein, "compatible" means that the component does not cause adverse affects to the curable composition (e.g., precipitation, flocculation, or other separation of the components), or to the cured coating (e.g., disruption of film continuity, phase separation, or loss of adhesion to the backing). Preferred thickeners for use in the curable coating compositions of the present invention are associative thickeners. An "associative" thickener is a polymeric compound having hydrophobic groups that associate with the dispersed polymer particles of the curable coating composition. This association is believed to result in adsorption of the thickener molecule onto the dispersed polymer particles.

A preferred thickener is a polyurethane available under the trade designation "Dexx 514" from Henkel Corp., Kankakee, Ill., as an aqueous dispersion having 40 wt-% solids. It is a high shear and low molecular weight thickener having a Brookfield viscosity of 3000 centipoise at 25° C. It is particularly desirable because it provides a significant increase in viscosity of the coating composition when used in small amounts.

For example, when used in an amount of about 0.6 wt-%, based on the total weight of the composition, the Brookfield viscosity of a dispersion of "NeoPac R-9699" urethane/acrylic polymer increases from about 100 centipoise to about 12,000 centipoise at 25° C.

An associative thickener, or mixture of associative thickeners, is present in the curable coating compositions of the present invention in an amount effective to increase the viscosity of the dispersions to provide coatings that do not sag. Preferably, an associative thickener, or mixture of associative thickeners, is present in the curable coating compositions of the present invention in an amount of less than about 1 wt-%, and more preferably, in an amount of about 0.05-0.8 wt-%, based on the total weight of the curable coating composition (including water).

Surfactants may be used in the curable coating compositions of the present invention to reduce foaming and to enhance leveling and wetting. This is important to provide smooth, uniform coatings. A wide variety of surfactants, i.e., surface-active agents, are suitable for use in the curable coating compositions of the present invention. Typically, additives that are suitable for use in water-based systems that perform the functions of a defoamer, leveling agent, and/or wetting agent, for example, are suitable. Suitable surfactants include, but are not limited to, flow control agents, wetting agents, dispersants, adhesion enhancers, defoamers, etc. Preferred surfactants are nonionic or anionic. Examples of preferred surfactants are available under the trade designa-

tion "Silwet L-7210" (a nonionic polyalkyleneoxide modified polydimethylsiloxane) from Osi Specialties, Inc., Danbury, Conn., "Surfynol 104PA" (2,4,7,9-tetramethyl-5-decyn-4,7-diol) from Air Products and Chemicals, Inc., Allentown, Pa., and "Triton GR-7M" (an anionic sulfosuccinate) from Union Carbide Chemicals and Plastics Company, Inc., Danbury, Conn.

A surfactant, or mixture of surfactants, is present in the curable coating compositions of the present invention in an amount effective to provide a smooth, uniform coating. Preferably, a surfactant, or mixture of surfactants, is present in the curable coating compositions of the present invention in an amount of about 0.1-3 wt-%, and more preferably, about 0.5-2 wt-%, based on the total weight of the curable coating composition (including water).

The low VOC curable coating compositions of the present invention can include other optional additives such as colorants, flattening agents, UV absorbers, UV scavengers, coupling agents, adhesion promoters, fillers, and the like, that are compatible with water-based systems. Any of these components, as well as any of the components listed above, can be used in various combinations, including two or more of each type of compound, to achieve desired results.

Colorants, such as pigments and dyes, suitable for use in water-based systems are well known in the art and can include, for example, carbon blacks, titanium dioxide, and the like. An example of a carbon black is that available under the trade designation "Carbon Black Aqualour 36B17" from Penn Color, Inc., Doylestown, Pa. Phosphorescent pigments, i.e., compounds that glow in the dark, are particularly desirable colorants. Suitable phosphorescent pigments include, for example, phosphorescent pigment available under the trade designation "Excite 2330LBY" from LJSR OPTONIX Inc., Hackensack, N.J. A pigment, or mixture of pigments, is typically used in an amount effective to provide the desired color, which is well known to one of skill in the art.

Flattening agents may be used in the curable compositions of the present invention to reduce the reflective characteristics (i.e., gloss) of the cured coating. Suitable flattening agents are those that are compatible with water-based systems. Particularly suitable flattening agents are silica flattening agents, which are available under the trade designations "Lo-Vel 27" and "Lo-Vel 275" (ultrafine amorphous silica) from PPG Industries, Inc., Pittsburgh, Pa. A flattening agent, or mixture of flattening agents, is typically used in an amount effective to provide the desired level of gloss to the cured coating, which is well known to one of skill in the art.

UV scavengers and UV absorbers may be used in the curable compositions of the present invention to enhance UV stability of a cured coating. Suitable UV scavengers and absorbers are those that are compatible with water-based systems. One particularly suitable UV scavenger is available under the trade designation "Tinuvin 123 (a bis(2,2,6,6-tetramethyl-4-piperidinyl)ester of decanedioic acid), which is the reaction product of 1,1-dimethylethylhydroperoxide and octane) from Ciba-Geigy Corporation, Tarrytown, N.Y. One particularly suitable UV absorber is available under the trade designation "Tinuvin 1130" (a substituted hydroxyphenyl benzotriazole) from Ciba-Geigy Corporation, Tarrytown, N.Y. A UV scavenger or UV absorber, or mixture of such compounds, is typically used in an amount effective to provide the desired UV stability, which is well known to one of skill in the art. Typically, these are added to the coating composition as a premix with the plasticizer to avoid precipitation.

Coupling agents can be used in the curable compositions of the present invention to enhance bonding of any frictional

particles, particularly those that are made of a ceramic material, applied to the surface of a coating formed from the coating composition or mixed within the coating composition. Suitable coupling agents are those that are compatible with water-based systems. One particularly suitable coupling agent is a titanate coupling agent available under the trade designation "Lica 38" (a methylacrylamide functional amine adduct of neopentyl(diallyl)oxy tri(dioctyl)pyrophosphatotitanate) from Kearich Petrochemicals, Inc., Bayonne, N.J. A coupling agent, or mixture of coupling agents, is typically used in an amount effective to provide the desired adhesion of the frictional particles, which is well known to one of skill in the art.

Many production advantages exist with the use of this water-based coating composition. For example, odor during coating and curing is dramatically diminished, and curing time and temperature are reduced when compared to conventional solvent-based systems. Conventional solvent-based systems may require several hours at about 120° C. for drying and curing. For certain compositions of the present invention, however, temperatures of about 70°-110° C. can be used for less than about one hour, and for other compositions, temperatures of about 20°-30° C. can be used, thereby resulting in significant energy savings. Solvent emissions may be reduced to the point where emission control equipment may not be necessary. Fire and explosion hazards may also be reduced because no organic solvents, such as VOC coalescing solvents, are added to the composition.

An adhesion promoter may be used in the curable coating compositions of the present invention to enhance adhesion of the cured coating to a desired material, such as a backing sheet typically used in abrasive articles and antiship products or other surfaces to which the coating may be applied. A wide variety of adhesion promoters that are compatible with water-based urethane/acrylic polymer systems are suitable for use in the curable coating compositions of the present invention. Suitable adhesion promoters include, but are not limited to, acrylic copolymers and aliphatic polyester urethanes. Preferred adhesion promoters are available under the trade designations "NeoCryl A-633" (an acrylic copolymer available as an aqueous emulsion with 42 wt-% solids, which adheres well to steel and aluminum surfaces as well as engineering plastics such as acrylonitrile/styrene/butadiene, which is available, for example, under the trade designation "Lustran" from Monsanto or "Cycloac" from General Electric Plastics of Parkersburg, W. Va., polystyrene elastomers, which is available, for example, under the trade designation "Styron Foam" from Dow Chemical, and blends of polystyrene and polyphenylene ether, which is available under the trade designation "Noryl" from General Electric Plastics) and "NeoTac XR-9621" (an aliphatic polyester urethane available as an aqueous dispersion with 38 wt-% solids, which adheres well to vinyl, polyester, and low density polyethylene), both of which are from Zeneca Resins Inc., Wilmington, Mass. Acrylic copolymers are particularly desirable because they provide adhesion to a variety of materials, such as those mentioned above, as well as quarry tiles and vinyl composition tiles typically used on flooring surfaces, upon curing the coating composition at room temperature (i.e., 20°-30° C.).

An adhesion promoter, or mixture of adhesion promoters, is present in the curable coating compositions of the present invention in an amount effective to improve adhesion to a desired material. Preferably, aliphatic polyester urethane adhesion promoters, or mixture of such adhesion promoters, are present in the curable coating compositions of the

present invention in an amount of about 2-20 wt-%, more preferably, about 2-10 wt-%, and most preferably, about 3-7 wt-%, based on the weight of the urethane/acrylic copolymer solids. Preferably, acrylic copolymer adhesion promoters, or mixture of such adhesion promoters, are present in the curable coating compositions of the present invention in an amount of about 25-145 wt-%, and more preferably, about 60-120 wt-%, based on the weight of the urethane/acrylic copolymer solids.

Once applied to a backing sheet, the time and temperature used in the process of curing a composition of the present invention can impact adhesion of the coating to the backing sheet on which it is coated. Preferably, to obtain a desirable coating, the coating composition is allowed to dry for a short period of time at a relatively low temperature, preferably for about 1-12 minutes at a temperature of less than about 45° C. It is then placed in a preheated oven set at a temperature greater than about 45° C. for less than about five minutes, preferably at a temperature of about 70°-80° C., for about 1-2 minutes. While the coated backing sheet is still in the oven, the temperature of the oven is raised to about 90°-110° C. over a short period of time, preferably over about 2-6 minutes. The oven is then maintained at this temperature for about 15-30 minutes. In this way, water is driven off slowly from the coating composition, thereby preventing the formation of bubbles and cracks. Furthermore, this allows for the formation of a strong bonding interaction with the backing sheet. By comparison, if the curable coating composition is exposed to a high temperature, such as 100° C., without initially slowly driving off the water, cracks can form. If the curable coating composition is exposed to a lower temperature, such as 20°-30° C., for a longer period of time, a uniform coating forms, but it does not typically adhere well to the backing sheet. Thus, to obtain a strong flexible coating that adheres well to backing sheets, it is desirable to slowly drive off the water at a low temperature and then heat the coated backing sheet to a temperature high enough to cure the coating. Alternatively, it has been discovered that acrylic copolymer adhesion promoters, such as that available under the trade designation "NeoCryl A-633" are particularly suitable for providing good adhesion for coatings cured at temperatures of about 20°-80° C., and preferably at about room temperature (i.e., 20°-30° C.).

The curable coating compositions of the present invention can be used as a paint, primer, edge sealer, or as a binder for holding frictional particles to antislip products such as friction surface sheet materials and nonskid or antislip sheet materials. Examples of such materials include, but are not limited to, friction surface sheet materials for use on smooth surfaces such as stair treads, skate boards, boat trailer fenders, diving boards, and surf boards, as well as on rough and irregular surfaces such as grooved metal ladder rungs, curved truck fenders, and curved stair nosing. Such materials are disclosed, for example, in U.S. Pat. Nos. 3,578,550 (Hoerner et al.) and 4,328,274 (Tarbutton et al.). Generally, antislip sheet materials include a backing sheet, frictional particles, and at least one binder to hold the frictional particles on the backing. Preferably, such products include a first layer of a binder material, a layer of frictional particles, and a second layer of a binder material. Typically, the first layer of binder material is referred to as a "make" coating and the second layer of binder material is referred to as a "size" coating. A layer of pressure sensitive adhesive can be coated on the surface of the backing sheet opposite the frictional particles and binder layers.

The curable coating compositions of the present invention can also be used as a binder for holding minerals, for

example, to conventional abrasive articles, such as to coated abrasive products (including structured abrasives, lapping films, and the like), and nonwoven abrasive products (including nonwoven abrasive pads), and bonded abrasive products (including grinding wheels, cutoff wheels, and honing stones). Coated abrasive products include a backing sheet, frictional particles (e.g., abrasive grain), and at least one binder to hold the frictional particles on the backing. Preferably, such products include a first layer of a binder material (i.e., the make coating), a layer of frictional particles, and a second layer of a binder material (i.e., the size coating). The coating compositions of the invention are particularly useful in film-backed coated abrasives, such as lapping films, and in coated abrasive articles to be used in lubricated environments or in low pressure and/or low temperature applications. Nonwoven abrasive products typically include an open porous lofty polymer filament structure having abrasive grain distributed throughout the structure and adherently bonded therein by a binder. Bonded abrasives typically include a shaped mass of abrasive grain held together by a binder. In each of these applications, the cured coating compositions of the present invention perform the function of the binder.

Referring to FIG. 1, antislip sheet material 10 (which could also be representative of a coated abrasive product) includes backing sheet 11, having upper surface 12 and lower surface 13. First layer 14 of first binder material (the "make" coating) is bonded to upper surface 12. Second layer 15 of second binder material (the "size" coating) overcoats first layer 14. A multitude of frictional particles 16, which is capable of withstanding pedestrian traffic without significant fracture, are uniformly distributed over upper surface 12 of backing sheet 11 and firmly bonded thereto by make coating 14 and size coating 15 so that the tops of frictional particles 16 project above the general plane of the exposed surface of size coating 15 to provide a friction surface. It should be noted that the size coating may cover some of the projecting parts of the frictional particles, because the size coating is applied over the frictional particles in making the sheet material. In that case, the top ends of the frictional particles will project above the plane of the top surface of the size coating with a layer of size coating of varying thickness covering the top ends to provide a protruberance consisting of a size coated abrasive particle. In use, the size coating can wear away to expose the projecting top end of the abrasive particle. The combined thickness of the make and size coatings 14 and 15 is sufficient to bond particles 16 thereto and to substantially resist particle loss under pedestrian use.

An optional layer 17 of pressure sensitive adhesive is coated on lower surface 13 of backing sheet 11 to facilitate attachment of the antislip sheet material (or coated abrasive product) to a substrate surface. Optionally, if the backing sheet, make coating, size coating, and pressure sensitive adhesive are transparent, either bottom surface 13 or top surface 12 of backing sheet 11 can be imprinted to provide a decorative design, message or other indicia to provide decoration as is disclosed in U.S. Pat. No. 4,328,274 (Tarbutton et al.). Preferably, if adhesive layer 17 is used, it is protected by an appropriate release liner 19, which can be formed from sheet material known for this purpose, such as silicone coated kraft paper and the like.

The make and size coatings can be formed from the same curable coating composition. Alternatively, the make and size coatings may be from two different coating compositions. For example, the make coating can include a plasticized acrylate polymer and the size coating can include the composition of the present invention. One skilled in the art

will understand the necessity of assuring effective adhesion of the make coating to the backing sheet and any added minerals or fillers, as well as adhesion of the size coating to the same minerals and the make coating itself. If the make coating and size coating include the composition of the present invention, the size coating typically includes a flattening agent and/or colorant as well as a UV scavenger and/or absorber. The coating weight of the make and size coatings will vary depending upon the size of the frictional particles, more binder being permitted with larger particles. The make and size coatings should be of a sufficient thickness to bond the particles, but not so thick as to obscure the particles and thereby diminish or eliminate friction surface. Typical coating weights are about 85-200 grams per square meter for the make coating and about 45-145 grams per square meter for the size coating.

The backing sheet is formed from sheet material known for this purpose, such as cloth, paper, nonwoven webs, polymeric film, fiber, metal sheets, as well as laminates or treated versions thereof. Examples include, but are not limited to, cloth or nonwovens of glass, polyester, polyamide, rayon, cotton, or combinations thereof, polymeric films of polyamide, polyvinyl chloride, polyethylene, polypropylene, or combinations thereof, biaxially oriented films of polyethylene terephthalate and polypropylene, annealed aluminum foil, polymethyl methacrylate and ethylene-methacrylic acid copolymers. Typically, the backing sheet need not have an extremely high degree of strength, although such strength is preferred. The backing sheet should, however, have sufficient strength to permit processing, i.e., coating and handling, and installation upon a substrate, and, if desired, removal from such substrate. The surface of the backing sheet can be primed or otherwise treated to improve adhesion to coatings thereon. Many known surface treatments can be used for this purpose.

A wide variety of frictional particles can be used in making the antislip and abrasive articles of the present invention. Suitable such particles include, but are not limited to, abrasive grain such as silicon carbide, fused aluminum oxide, ceramic aluminum oxide, heat treated aluminum oxide, white aluminum oxide, alumina zirconia, diamond, ceria, cubic boron nitride, garnet, sol-gel derived abrasive grain, and the like, as well as cork, rubber, glass, and polymeric particles made from polyester, urea-formaldehyde, melamine, acrylic, polyalkyl diglycol carbonate, and phenolic resins. The particles can be transparent or opaque. They can be regularly shaped or irregularly shaped, with or without sharp edges (although sharp edges are preferred for abrasive articles). The term "frictional particles" also encompasses single particles that are bonded together to form an agglomerate. The particle size range can vary, depending on the particular use, which is well known to one of skill in the art.

A wide variety of conventional pressure sensitive adhesives can be used. The one selected should have excellent adhesion to the chosen backing sheet. It should also have excellent initial adhesion to ensure adequate adhesion when the antislip material is first placed on a surface. Preferably, it is selected to have a relatively high degree of cohesive strength to prevent splitting, if the antislip sheet material is to be removed from the substrate. Also, for use on irregular surfaces, it should have a relatively low degree of recovery or elastic memory to reduce the possibility of the sheet material pulling away from the irregular surface once it has been adhered.

The antislip and coated abrasive articles of the present invention can be prepared by conventional techniques that

are known to one of skill in the art. For example, for antislip sheet materials and coated abrasive products a curable coating composition can be applied to a backing sheet by brushing, roll coating, extrusion coating, curtain coating, spraying, knife coating, and the like. Frictional particles can then be applied to this first layer of binder (i.e., the make coating) by a number of known methods such as the methods known in the abrasive making art. One preferred method of coating the frictional particles on the backing sheet is by drop coating wherein the frictional particles are permitted to fall through the air onto the freshly coated surface of the backing sheet so as to be uniformly distributed across the coated surface. Thereafter, the make coating can be cured, or the size coating can be applied immediately and both coatings cured simultaneously.

The coating compositions of the present invention can also be used in antislip products without the need for a backing sheet. That is, a composition of the present invention can be cured to form a free-standing coating, and a layer of adhesive may be applied to one surface of the free-standing cured coating. Such a free-standing cured coating is typically more conformable than if a backing sheet were used. Such a free-standing cured coating can be embossed (either before or after formation of the coating) or include frictional particles mixed therein. To prepare a free-standing cured coating, the curable coating composition is coated on a nonadherent surface, which can be an embossing tool made of polyethylene or untreated polyester, for example, and cured. A layer of adhesive, which can be on a release liner, is then applied to the cured coating. The release liner, adhesive, and cured coating is then removed from the nonadherent surface as a unitary structure. This free-standing cured coating can then be applied directly to a substrate with the intervening layer of adhesive but no backing sheet.

Referring to FIG. 2, antislip sheet material 20 includes free-standing coating 21 having upper surface 22 and lower surface 23. A layer 27 of pressure sensitive adhesive is coated on lower surface 23 of free-standing coating 21 to facilitate attachment of the antislip sheet material to a substrate surface. Preferably, adhesive layer 27 is protected by appropriate release liner 29, which can be formed from sheet material known for this purpose, such as silicone coated kraft paper and the like.

The following examples are offered to further illustrate the various specific and preferred embodiments and techniques of the present invention. It should be understood, however, that many variations and modifications can be made while remaining within the scope of the present invention.

## EXAMPLES

### Preparation of Coating Compositions

Each of the coating compositions described in the following examples was prepared by adding in sequence to a suitable container the listed components in the amounts identified. Each addition was followed by mixing with a standard low shear laboratory propeller-type mixer at medium speed for approximately 5-10 minutes or until the component was blended into the mixture. If a crosslinker was added to the mixture, prior to its addition, the composition was mixed for about 1 hour, after which time the crosslinker was added followed by a final mixing of about 5-10 minutes.

Unless otherwise specified, the backing sheet on which the compositions were coated was an aziridine-primed poly-

ester film. Aziridine-primed polyester film was manufactured as described in U.S. Pat. No. 5,057,371 (Canty et al.) using the aziridine treatment solution of U.S. Pat. No. 4,749,617 (Canty), Example 1 modified to include a water-based urethane polymer (as shown in Example 2 of U.S. Pat. No. 4,749,617). Thus, sufficient treatment solution containing 1.8 wt-% water-based urethane polymer, 0.2 wt-% sulfonated polyester polymer, 0.4 wt-% XAMA-7 polyfunctional aziridine, 0.16 wt-% Triton X-100 (Rohm and Haas, Philadelphia, Pa.), and 97.44 wt-% water was applied to polyester film to achieve a dry thickness of 40 nm.

The composition was coated onto the aziridine-primed polyester film, unless otherwise specified, to a wet thickness of about 0.30 mm, and generally to a wet thickness within a range of about 0.20 mm to about 0.38 mm, unless otherwise specified.

#### Comparative Example A

A coating composition was prepared from 200 grams of "NeoPac R9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Silwet L-7210" non-ionic polyalkylene oxide modified silicone surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), and 5.7 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.0 gram of "DSX-1514" thickener as purchased and 4.7 grams of 60° C. water). Once coated on the aziridine-primed polyester film, the composition was dried by heating in an oven at 64° C. for 15 minutes. A nonuniform brittle film resulted using a thickener with the urethane/acrylic copolymer in the absence of a plasticizer and a crosslinker.

#### Comparative Example B

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), and 4.0 grams of "Pycal 94" polyoxyethylene aryl ether plasticizer ( $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_4-\text{C}_6\text{H}_5$ ). Once coated on the aziridine-primed polyester film, the composition was dried by heating in an oven at 64° C. for 15 minutes. A uniform but weak coating was formed using only a plasticizer with the urethane/acrylic copolymer.

#### Comparative Example C

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), and 16.0 grams of "Pycal 94" polyoxyethylene aryl ether plasticizer. Once coated on the aziridine-primed polyester film, the composition was dried by heating in an oven at 64° C. for 15 minutes. This coating was uniform and stronger than that of Comparative Example B and flexible, but it lacked acceptable durability for the proposed uses.

#### Example 1

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Pycal 94" plasticizer, 4.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 7.1 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.2 grams of "DSX-1514" thickener as purchased and 5.9 grams of 60° C. water), and 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker (pentaerythritol-tris-(B-(N-aziridinyl)

propionate). Once coated on the aziridine-primed polyester film, the composition was cured by drying it for 20 minutes at 93° C. A durable, flexible coating that adhered well to the backing sheet was formed using a plasticizer, crosslinker, and the urethane/acrylic copolymer.

#### Example 2

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Hypermer IL-2718" polyoxyethylene aryl ether plasticizer ( $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_6-\text{C}_6\text{H}_5$ ), 4.0 grams of "Silwet L-7210" non-ionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 7.1 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.2 grams of "DSX-1514" thickener as purchased and 5.9 grams of 60° C. water), and 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. Once coated on the aziridine-primed polyester film, the composition was cured by drying it for 20 minutes at 93° C. A durable, flexible coating that adhered well to the backing sheet was formed.

#### Example 3

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Hypermer IL-2719" polyoxyethylene aryl ether plasticizer ( $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_8-\text{C}_6\text{H}_5$ ), 4.0 grams of "Silwet L-7210" non-ionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 7.1 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.2 grams of "DSX-1514" thickener as purchased and 5.9 grams of 60° C. water), and 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. Once coated on the aziridine-primed polyester film, the composition was cured by drying it for 20 minutes at 93° C. A durable, flexible coating that adhered well to the backing sheet was formed.

#### Example 4

A coating composition was prepared from 200 grams of "NeoPac R9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Hypermer IL-2707" plasticizer ( $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_{10}-\text{C}_6\text{H}_5$ ), 4.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 7.1 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.2 grams of "DSX-1514" thickener as purchased and 5.9 grams of 60° C. water), and 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. Once coated on the aziridine-primed polyester film, the composition was cured by drying it for 20 minutes at 93° C. A durable, flexible coating that adhered well to the backing sheet was formed.

#### Example 5

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Pycal 94" plasticizer, 4.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 7.1 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.2 grams of "DSX-1514" thickener as purchased and 5.9 grams of 60° C. water), 2.0 grams of "Aqualour 36B17" carbon black dispersion ("Aqualour 36B17" carbon black as purchased

diluted to 50% solids in water), and 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. Once the composition was coated on the aziridine-primed polyester film, sharp abrasive mineral was scattered by hand onto the wet coating in a generally uniform random manner to a weight of abrasive of about 209 g/m<sup>2</sup>. The composition was then cured by drying it for 20 minutes at 93° C. A durable, flexible coating that adhered well to the backing sheet and mineral was formed.

#### Example 6

A coating composition was prepared from 500 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant dispersion solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 1.0 gram "Surfynol 104PA" nonionic surfactant, 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. Once coated on the aziridine-primed polyester film, this composition was allowed to stand at room temperature (about 22° C.) for 5 minutes and then heated in an oven at 74° C. for 1 minute. The temperature of the oven was then raised to 102° C. over about 5 minutes, and maintained at this temperature for 20 minutes for further curing of the coating. A durable, flexible coating that adhered well to the backing sheet was formed.

#### Example 7

A coating composition was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 4.0 grams of "Pycal 94" plasticizer, 4.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 7.1 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.2 grams of "DSX-1514" thickener as purchased and 5.9 grams of 60° C. water), and 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. After coating this composition onto the aziridine-primed polyester film, CarboProp 20/40 ceramic beads from Carbo Ceramics, Inc., New Iberia, La., were scattered by hand onto the wet coating in a generally uniform random manner to a weight of abrasive of about 775 g/m<sup>2</sup>. The composition was cured by drying it for 5 minutes at 66° C. and subsequently for 20 minutes at 93° C. A durable, flexible make coating that adhered well to the backing sheet and mineral was formed.

A second coating composition (i.e., the size coating) was prepared from 200 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer, 4.0 grams of "Pycal 94" plasticizer, 4.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 2 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 0.35 gram of "DSX-1514" thickener as purchased and 1.65 grams of 60° C. water), 4.0 grams of "XAMA-7" polyfunctional aziridine crosslinker, and 1 gram of "Lica 38J" coupling agent. This composition was coated on the cured construction having a make coating and ceramic beads and then heated again for 20 minutes at 93° C.

#### Examples 8 and 9

A coating composition was prepared from 500 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer

(40% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 1.0 gram of "Surfynol 104PA" nonionic surfactant, and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. After coating this composition onto the aziridine-primed polyester film, either sharp abrasive mineral as used in Example 5 (Example 8) or carbo prop 20/40 ceramic beads as used in Example 7 (Example 9) were scattered by hand onto the wet coating in a generally uniform random manner to a weight of about 210 g/m<sup>2</sup> (Example 8) or 775 g/m<sup>2</sup> (Example 9). The compositions were both cured by drying for 5 minutes at 21° C., then for 1 minute at 74° C., then for 5 minutes while the temperature was increased from 74° C. to 102° C., and finally for 20 minutes at 102° C. Durable, flexible make coatings that adhered well to the backing sheet and mineral were formed.

A second coating composition (i.e., the size coating) was prepared from 500 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 1.0 gram of "Surfynol 104PA" nonionic surfactant, and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. This composition was coated on the cured constructions with sharp abrasive mineral (Example 8) or the ceramic beads (Example 9) and then cured by heating the composition as described for the make coating.

#### Examples 10 and 11

A coating composition was prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 1.0 gram of "Surfynol 104PA" nonionic surfactant, and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. After coating this composition onto the aziridine-primed polyester film, either sharp abrasive mineral as used in Example 5 (Example 10) or carbo prop 20/40 ceramic beads as used in Example 7 (Example 11) were scattered by hand onto the wet coating in a generally uniform random manner to a weight of about 210 g/m<sup>2</sup> (Example 10) or 775 g/m<sup>2</sup> (Example 11). The compositions were both cured by drying for 5 minutes at 21° C., then for 1 minute at 74° C., then for 5 minutes while the temperature was increased from 74° C. to 102° C., and finally for 20 minutes at 102° C. Durable, flexible make coatings that adhered well to the backing sheet and mineral were formed.

A second coating composition (i.e., the size coating) was prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams

of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 1.0 gram of "Surfynol 104PA" nonionic surfactant, and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. This composition was coated on the cured constructions with sharp abrasive mineral (Example 10) or the ceramic beads (Example 11) and then cured by heating the composition as described for the make coating.

#### Example 12

A coating composition was prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased diluted to 50% in water), 3.0 grams of "Triton GR-7M" anionic surfactant, 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 5.0 grams "Aqualour 36B17" carbon black pigment ("Aqualour 36B17" carbon black as purchased diluted to 50% solids in water), and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. After coating this composition onto the aziridine-primed polyester film, sharp abrasive mineral as used in Example 5 was scattered by hand onto the wet coating in a generally uniform random manner to a weight of about 200 g/m<sup>2</sup>. The coated sample was allowed to stand at room temperature (22° C.) for 5 minutes. It was then heated in an oven at 85° C. for 1 minute. The temperature of the oven was then raised to 102° C. over about 2 minutes, and maintained at this temperature for 5 minutes for further curing of the coating. A durable, flexible make coating that adhered well to the backing sheet and mineral was formed.

A second coating composition (i.e., the size coating) was prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased diluted to 50% in water), 3.0 grams of "Triton GR-7M" anionic surfactant, 2.9 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 0.5 gram of "DSX-1514" thickener as purchased and 2.4 grams of 60° C. water), 10.0 grams "Aqualour 36B17" carbon black pigment ("Aqualour 36B17" carbon black as purchased diluted to 50% solids in water), and 15.0 grams of "Lo-Vel 275" ultrafine amorphous silica. This composition was coated on the cured construction with sharp abrasive mineral and then cured by heating the composition as described for the make coating.

#### Example 13

A coating composition was prepared from 450 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 50 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams

of "Silwet L-7210" nonionic surfactant solution C "Silwet L-7210" surfactant as purchased diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. After coating this composition onto the aziridine-primed polyester film, it was cured by drying for 20 minutes at 66° C. A durable, flexible make coating that adhered well to the backing sheet and mineral was formed.

#### Example 14

A coating composition was prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), a premixed solution of 10.0 grams of "Pycal 94" plasticizer with 4.0 grams of "Tinuvin 1130" UV absorber and 2.0 grams of "Tinuvin 123" UV scavenger, 10.0 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased diluted to 50% in water), 3.0 grams of "Triton GR-7M" anionic surfactant, 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 5.0 grams "Aqualour 36B17" carbon black pigment (50% solids in water), and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. After coating this composition onto the aziridine-primed polyester film, sharp abrasive mineral as used in Example 5 was scattered by hand onto the wet coating in a generally uniform random manner to a weight of about 210 g/m<sup>2</sup>. The composition was cured by drying for 5 minutes at 21° C., then for 1 minute at 85° C., then for 5 minutes while the temperature was increased from 85° C. to 102° C., and finally for 20 minutes at 102° C. A durable, flexible make coating that adhered well to the backing sheet and mineral was formed.

#### Example 15

A coating composition was prepared as in Example 14 except as follows: no "Tinuvin 1130" UV absorber or "Tinuvin 123" UV scavenger was added; no "Aqualour 36B17" carbon black pigment was added; 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica was added and dispersed well; to 50 grams of this composition were added 60 grams of "Excite 2330LB" phosphorescent pigment and the whole composition was mixed for about 1 minute to achieve uniform dispersion of the pigment into the coating composition. After coating this composition onto the aziridine-primed polyester film, the coated sample was allowed to stand at room temperature (about 22° C.) for 5 minutes. It was then placed in an oven and heated for 1 minute at 74° C. The temperature of the oven was then increased from 74° C. to 102° C. over about 5 minutes, and maintained for 20 minutes at 102° C. for further curing of the composition. A durable, flexible make coating that adhered well to the backing sheet was formed.

#### Examples 16-24

For each of Examples 16-24, coating compositions were prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased

diluted to 50% in water), 8.5 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.5 grams of "DSX-1514" thickener as purchased and 7.0 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 5.0 grams "Aqualour 36B17" carbon black pigment "Aqualour 36B17" carbon black as purchased diluted to 50% solids in water), 1.0 gram of "Surfynol 104PA" nonionic surfactant, and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker.

Film substrates were knife-coated with this coating composition with the knife gap set at about 0.30 mm resulting in wet film thicknesses of about 0.25-0.38 mm. Once coated on the backing sheet of interest (see below), the composition was cured by drying the constructions for 1-12 minutes at 21° C., then for 1-2 minutes at 74° C., then for 2-6 minutes while the temperature was increased from 74° C. to 102° C., and finally for 15-30 minutes at 102° C. In each example, durable, flexible coatings that adhered well to the backing sheet were formed.

The following backing sheets were coated with the composition described above to the listed thickness: Example 16, polyethylene terephthalate (PET) film treated with a 500 watt corona discharge in air as is known in the art; Example 17, PET film treated with an aqueous aziridine priming agent as described above; Example 18, polyvinyl chloride (PVC) film; Example 19, PET film treated with a reducing flame as described in U.S. Pat. No. 3,431,135, Example 5, except that the fuel was natural gas instead of propane, the burner-to-film distance was 5 mm, and the film transport speed across the flame was 80 meters/minute; Example 20, a structured polymeric release (nonadherent) surface such as that available under the trade designation "Ultracast Madagascar" from SD Warren Co., Boston, Mass.; Example 21, aluminum foil treated on one side with "S-311" surface treatment, available from ALCOA Chemicals Division, Pittsburgh, Pa. (the treated side was coated with the composition described above); Example 22, aluminum foil from Example 21, except the untreated side was coated with the composition described above after wiping with a paper towel to smooth the surface; Example 23, 0.025 mm "Saran Wrap" polyvinylidene chloride film (Dow Chemical Co., Midland Mich.); Example 24, 0.075 mm "Melinex" Type 454 PET film (ICI Americas, Inc.) having a polyacrylic acid copolymer prime coating.

#### Example 25

This example demonstrates the preparation of a nonwoven grinding wheel. A 15 mm thick low-density nonwoven web weighing 120 g/m<sup>2</sup> was formed from 38 mm staple length 13 denier nylon-6,6 fibers on a web forming machine available under the trade designation "Rando Webber" (Cufiator Company, Rochester, N.Y.). The resulting low density web was roll-coated with a prebond resin containing 110 parts of a resole phenol formaldehyde liquid resin (a base catalyzed phenol formaldehyde resin with a phenol to formaldehyde ratio of 1:1.6 and an ultimate nonvolatile content of 70%), 15 parts of isopropyl alcohol, 3 parts of antifoaming agent available under the trade designation "Q2" from Dow Coming, Midland, Mich., and 1 part of a black colorant available under the trade designation "Aqualour 36B17" "Aqualour 36B17" carbon black as purchased diluted to 50% solids in water) to provide a dry add-on weight of 87 g/m<sup>2</sup>. The prebond resin was cured to a nontacky condition by passing the coated nonwoven web through a convection oven maintained at 140° C. for a residence time of about 7 minutes. The resultant prebonded nonwoven web was about 12 mm thick and weighed about 207 g/m<sup>2</sup>.

In order to make a nonwoven abrasive grinding wheel, rectangular pieces of the above prebonded nonwoven web, each piece measuring 229 mm×280 mm, were coated with an abrasive resin slurry containing 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10 grams of "Pycal 94" plasticizer, 10 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased diluted to 50% in water), 17 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 3 grams of "DSX-1514" thickener as purchased and 14 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 1.0 gram of "Surfynol 104PA" nonionic surfactant, 83 grams of 150 grit silicon carbide abrasive, 83 grams of 180 grit silicon carbide abrasive, and 10 grams of "XAMA-7" polyfunctional aziridine crosslinker. A conventional two roll coater equipped with hard rubber rolls was used to coat the slurry onto the web. The roller nip pressure was adjusted to enable a wet add-on of 2000 g/m<sup>2</sup> of the web. The resin coating and abrasive particles were observed to be uniformly distributed throughout the three dimensional matrix of the nonwoven prebond. The slurry-coated nonwoven was heated in an oven at 74° C. for a period of 3 minutes in order to partially evaporate the water in the coating, thereby increasing the viscosity of the coating and preventing the migration of the coating components during the subsequent process step.

A slab was prepared from twelve pieces of the uncured coated web which were stacked one upon the other and placed in a vacuum platen press preheated to 135° C., compressed to 25 mm Hg under vacuum and held under pressure for 45 minutes at the platen temperature while applying suction to the enclosed space in the platen. The cured slab was removed from the platen press, allowed to degas in a 135° C. oven at atmospheric pressure for 90 minutes, and finally allowed to cool to room temperature. A 25 mm thick abrasive wheel having an outer diameter of 203 mm and an arbor hole of 31.8 mm was die cut from the cured slab. The wheel had a measured density of 0.623 g/cm<sup>3</sup>.

The wheel was tested for performance by fixing the wheel onto a lathe, rotating the wheel at 2000 revolutions per minutes (rpm), and urging a preweighed 1018 steel coupon measuring 30 mm×100 mm against the radial edge of the wheel for 1 minute after which the weight loss from the metal coupon was determined. Five such 1 minute periods of testing were done before the lathe was stopped, the wheel removed and its weight loss determined. The cumulative weight loss of the test coupon was 0.35 grams; the weight loss from the wheel was 0.05 gram. The resulting efficiency index, the ratio of cut (coupon weight loss) to wear (wheel weight loss) was therefore determined to be 7.

#### Example 26

This example demonstrates the preparation of a low density, nonwoven abrasive pad. A continuous three dimensionally undulated interengaged autogenous bonded web was formed according the disclosure in U.S. Pat. No. 4,227,350 (Fitzer) from nylon-6. The web was 10 mm thick with fiber diameter varying between 0.3 to 0.4 mm. Web weight was about 400 g/m<sup>2</sup>. Pieces of this web measuring approximately 25 cm×25 cm were roll-coated to a wet add-on weight of 50 grams with a binder resin containing 475 grams of "NeoRez R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10 grams of "Pycal 94"

plasticizer, 10 grams of "Silwet L-7210" nonionic surfactant solution "Silwet L-7210" surfactant as purchased diluted to 50% in water), 22.4 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 4.0 grams of "DSX-1514" thickener as purchased and 18.4 grams of 60° C. water), 7.5 grams of "Lo-Vel 275" ultrafine amorphous silica, 1.0 gram of "Surfynol 104PA" nonionic surfactant, 5 grams of "Aqualour 36B17" carbon black pigment "Aqualour 36 B17" carbon black as purchased diluted to 50% solids in water), and 10.0 grams of "XAMA-7" polyfunctional aziridine crosslinker. The coated web was allowed to stand for 5 minutes at room temperature and then sprayed with dry 60 grit aluminium oxide mineral from each side of the web such that the mineral add-on was about 25 grams total. The mineral was observed to be uniformly distributed throughout the matrix of the web filaments. The web was then cured at 108° C. for 30 minutes. The abrasive was firmly adhered to the cured resin, and the uniform black color of the web indicated that the binder resin was uniformly coated over the opaque white fibers.

Performance of the cured coated web was determined with a Schiefer Abrasion Testing Machine as described in American Society of Testing Methods D4158 (1982). The apparatus as shown in FIG. 2 of ASTM D4158-82 was modified by replacing the upper abrading support and the lower specimen support with flat stainless steel discs 4 inches in diameter (upper) and 5 inches in diameter (lower) and  $\frac{3}{16}$  inch thick. The centers of rotation of the two supports are not colinear, being horizontally displaced by approximately 1 inch. The rotation of the two discs is in the same direction; the rotational speed of the two discs is approximately 250 rpm but is slightly different thus causing a grinding action between the two. Because the supports are horizontally offset, the pad overlaps the sample a little less than half way.

Discs measuring 100 mm diameter were die cut from the cured web and mounted onto the machine to test performance by abrading a standard hard acrylic plastic disc also mounted onto the machine. A preweighed disc was attached to the upper turntable of the machine via a "Dual-Lock" SJ3442 Type 170 tape available from the 3M Company, St. Paul, Minn. under the trade designation "Scotch-Mate". A preweighed 100 mm diameter poly(methylmethacrylate) disc 3.18 mm thick was attached to the bottom turntable of the machine using a double faced foam tape. The plastic disc is available under the trade designation "Acrylite" from American Cyanamid Company, Wayne, N.J., and has a Rockwell M Ball Hardness in the range of 90-105. Water was dripped on the acrylic disc at the rate of 40-60 drops per minute while grinding. The plastic disc was ground by lowering the upper turntable and initiating the revolution of both turntables. After 5000 revolutions the test was stopped and both the plastic disc and the nonwoven disc are weighed. The weight loss from both the sample and the workpiece were determined. The average weight loss from the acrylic test disc over 5 test runs was 0.77 gram. The average weight loss from the samples of nonwoven abrasive web over the same tests was 0.46 gram.

#### Example 27

This example demonstrates a macro-textured antislip coating. A coating composition was prepared from 12.35 kg of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 0.65 kg of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 260 grams of "Pycal 94" plasticizer, 260 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet

L-7210" surfactant as purchased diluted to 50% in water), 78 grams of "Triton GR-7M" anionic surfactant, 131 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 23 grams of "DSX-1514" thickener as purchased and 108 grams of 60° C. water), 130 grams "Aqualour 36B17" carbon black pigment "Aqualour 36B17" carbon black as purchased diluted to 50% solids in water), and 260 grams of "XAMA-7" polyfunctional aziridine crosslinker.

Using the tool described in U.S. Pat. No. 5,435,816 (Spurgeon et al.), a macro-textured polyethylene/polypropylene film to which the coating composition of the present invention does not adhere, was knife-coated with this composition to a wet thickness of about 43 mm, followed by drying for 2-6 minutes at 66° C. and then at 10-20 minutes at 85° C. A laminated adhesive (i.e., a pressure sensitive adhesive layer laminated on a release liner) available under the trade designation "Scotch 468" from the 3M Company, St. Paul, Minn., was laminated to this embossed coating. This construction of the coating of the present invention with a layer of adhesive and a release liner was then removed from the macro-textured film and ready for application to a substrate.

#### Examples 28-29

A coating composition was prepared from 12.35 kg of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 0.65 kg of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 260 grams of "Pycal 94" plasticizer, 260 grams of "Silwet L-7210" nonionic surfactant solution ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 78 grams of "Triton GR-7M" anionic surfactant, 131 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 23 grams of "DSX-1514" thickener as purchased and 108 grams of 60° C. water), 130 grams "Aqualour 36B17" carbon black pigment "Aqualour 36B17" carbon black as purchased diluted to 50% solids in water), and 260 grams of "XAMA-7" polyfunctional aziridine crosslinker. Prior to application of the coating composition, 120 grams of this composition was mixed with 18 grams of 500 grit silicon carbide (Example 28) or 12 grams of 220 grit alum A (fused aluminum oxide mineral) (Example 29).

Each of these compositions was knife-coated on the macro-textured film to increase the antislip properties as described in Example 27 to a wet thickness of about 38 mm, followed by drying for 2-6 minutes at 66° C. and then at 10-20 minutes at 85° C. The laminated pressure sensitive adhesive described in Example 27 was laminated to this embossed coatings. These constructions of the coating of the present invention with a layer of adhesive and a release liner were then removed from the macro-textured film and ready for application to a substrate.

#### Example 30

A coating composition was prepared from 475 grams of "NeoPac R-9699" water-based urethane/acrylic copolymer (40% solids in water), 25 grams of "NeoPac R-9621" aliphatic polyester urethane adhesion promoter (38% solids in water), 10.0 grams of "Pycal 94" plasticizer, 10.0 grams of "Silwet L-7210" nonionic surfactant ("Silwet L-7210" surfactant as purchased diluted to 50% in water), 3.0 grams of "Triton GR-7M" anionic surfactant, 5.7 grams of "DSX-1514" polyurethane thickener dispersion (prepared by premixing 1.0 gram of "DSX-1514" thickener as purchased and 4.7 grams of 60° C. water), and 10.0 grams "Aqualour

greater than about 0.5. The cured coating of Examples 7-11 and 31 were evaluated using this test and all passed.

#### Flexibility Tests

A Folding Endurance Tester available from Tinius Olsen Testing Machine Co., Willow Grove, Pa., was used to determine the flex fatigue resistance of the samples. Samples were cut to 12.7 cm×1.27 cm and were flexed 4500 cycles (270° per cycle; 180 cycles per minute) with a 0.91 kg load. A sample passed if there was no delamination of the coating from the backing sheet, less than about 5% mineral loss for samples with mineral coated thereon, or no cracking of the coating or delamination from the backing sheet. The cured coating of Example 10 was evaluated using this test and it passed.

#### Tensile Strength Tests

Free-standing coating of the inventive coating was prepared by coating the make coat solution of Example 10 on 2.5 cm×15.2 cm strips of untreated PET film. The coating does not adhere well to untreated PET. Thus, after curing, the coating could be gently peeled off the PET film to provide a free-standing coating for tensile testing. A standard Instron Tensile Tester, equipped with a jaw separation of 11.4 cm and set to run at a crosshead speed of 30.5 cm/minute, was used for tensile testing. Prior to testing, the thickness of each sample was determined with a micrometer. Tensile strength and elongation at the point of break were recorded. The tensile strength and elongation of the cured coating of Example 10 (make coating) were 28.3 MPa and 112% respectively.

The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims. The disclosures of all patents, patent applications, and documents are incorporated herein by reference.

#### What is claimed:

##### 1. An article comprising:

(a) a cured binder prepared from a curable water-based coating composition comprising:

- (i) a urethane/acrylic copolymer having a Tg greater than about 50° C.;
- (ii) a polyoxyethylene aryl ether plasticizer;
- (iii) an alkaline-stable crosslinker; and
- (iv) water;

wherein the curable water-based coating composition includes less than about 5 wt-% volatile organic compounds, based on the total weight of the composition; and

##### (b) a multitude of friction heating particles.

2. The article of claim 1 wherein the friction heating particles comprise abrasive grain.

3. The article of claim 2 which is a coated abrasive product.

4. The article of claim 2 which is a bonded abrasive product.

5. The article of claim 2 which is a nonwoven abrasive product.

6. The article of claim 1 which is an antislip sheet material.

7. The article of claim 1 further including a backing sheet having an upper surface and a lower surface with the binder coated on the upper surface.

##### 8. The article of claim 7 wherein the binder comprises:

(a) a first layer comprising a first binder material prepared from the curable water-based coating composition bonded to the upper surface; and

(b) a second layer comprising a second binder material prepared from the curable water-based coating composition bonded to the exposed surface of the first layer.

9. The article of claim 7 further including a layer of pressure sensitive adhesive coated on the lower surface of the backing sheet.

10. The article of claim 1 wherein the polyoxyethylene aryl ether plasticizer is present in an amount of about 1-10 wt-% based on the weight of polymer solids.

11. The article of claim 1 wherein the curable water-based coating composition further includes an adhesion promoter.

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